Thermochemistry in fluoro-solvents.

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Award date:
1968

Awarding institution:
University of Bath

THERMOCHEMISTRY IN FLUORO-SOLVENTS

submitted by

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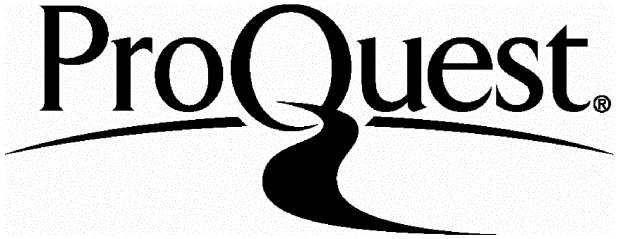
for the Degree of

Doctor of Philosophy

of the Bath University of Technology

June, 1968.



The work described in this thesis is original, except where specifically stated and has not been submitted for a degree at any other university.

I wish to thank Dr. A. A. Woolf for his constant advice and guidance and the Science Research Council for providing maintenance and equipment grants.

G. W. Richards.

C O N T E N T S

LIST OF DIAGRAMS

SUMMARY

Liquid phase fluorination methods of reaction calorimetry have been established using (1) a bromine-bromine trifluoride mixture and (2) fluorosulphuric acid. The heat of formation of (1) was obtained by measuring the heats of reaction with molybdenum and potassium iodate, bromide, persulphate and sulphate. A consistent heat of formation of the mixture was obtained and this value used to determine unknown heats of formation, e.g. antimonic and stannic fluorides.

The heat of formation of potassium fluorosulphate was required in the scheme to determine a value for the bromine-bromine trifluoride mixture. The value for potassium fluorosulphate was obtained by reaction calorimetry in fluoro-sulphuric acid. The work in this solvent was extended and the heats of formation of sodium, cupric, nitronium, nitrosonium fluorosulphates were obtained. The heats of formation of other fluorosulphates were predicted via heat cycles. The proximity of values for hydrogen and fluoro-sulphates was an important empirical observation.

The heats of formation of fluoro and chloro- sulphuric acids were determined and the values obtained combined with free energy functions to calculate possible dissociations of the acids. The theoretical values were compared with experimental observations.

The heats of formation of a series of acids and bases in bromine trifluoride were measured. From the heats of neutralisation of these acids and bases the heats of formation of several ternary complexes were obtained. In addition, values were obtained for heat of autoionisation of bromine trifluoride.

INTRODUCTION

Thermodynamic data are needed to predict reaction possibilities of fluoro-compounds, in particular their fluorinating ability. The establishment of thermochemical techniques could be an important part of this process especially since entropy and specific heat data can be estimated or calculated statistically, and would yield results of theoretical and practical interest.

At present there is a sparcity of thermodynamic data on fluorine compounds. In a recent exhaustive literature survey[1] on the heats of formation of inorganic fluorine compounds, values had only been determined for approximately a third of the binary compounds. Although many of the remainder can be estimated such values are probably uncertain. Even the reliability of existing data for some binary fluorides, for example those determined by gas-solid equilibration, is questionable. Data on ternary and quaternary compounds are even sparser.

This situation which restricts a quantitative consideration of fluorine chemistry can be attributed to the lack of generally accessible calorimetric techniques. The main methods used to date to determine the heats of formation of fluorides are:

1) Bomb Calorimetry.

The recent developments of fluorine[2] and nitrogen trifluoride[3] bomb calorimetry in metal apparatus and the simpler lower pressure fluorine calorimeter made of glass, have provided precision data approaching that of oxygen bomb calorimetry. Fluorine bomb calorimetry has been described,

developed and extensively used by Hubbard[2] and is now a well established method for complete fluorination reactions or when the products are easily analysed. However the analysis involved in this type of calorimetry may be tedious and time consuming. Not all fluorides can be formed under these conditions, some higher fluorides may be unstable whilst others may not form completely because of surface barriers. Complex fluorides in particular may be difficult to form quickly in heterogeneous reactions with fluorine.

2) Fluorine flame calorimetry.

This has limited application. a) CH_4 and F_2 to obtain the heat of formation of CF_4[4]. b) $H_2 + F_2$ for the heat of formation of hydrogen fluoride[5].

3) Explosion reaction calorimetry[6].

Heats of explosion also has limited application, some examples of its use are (a) H_2Se and H_2Te[21] and (b) the heats of formation of chlorine substituted methanes[22].

4) Reaction calorimetry.

The only two liquids used to any extent for fluoride calorimetry have been aqueous solutions and aqueous hydrogen fluoride.

a) Hydrolysis reactions.

These are only suitable for fluorides which are rapidly and quantitatively hydrolysed[7] e.g. $IF_5 + 6KOH = KIO_3 + 5KF + 3H_2O$ from which reaction the heat of formation of IF_5 can be obtained. This technique is only satisfactory for a few fluorides as many are either inert or alternatively yield poorly defined hydrolysis products, thus rendering the method impracticable.

b) Aqueous hydrofluoric acid.

This is only suitable for fluorides which form stable fluoro-acids and hence has only limited application.

Many complex acids of intermediate stability cannot be handled in either solvent so Woolf[8] suggested the use of more reactive non-aqueous fluoride solvents for solution calorimetry. Although the results in these solutions may not be as precise as those from fluorine bomb calorimetry they would be sufficiently accurate for use in conjunction with most of the available thermochemical data. It is important that completely independent techniques should be available to reveal any systematic errors in a particular technique. Consistent results are sometimes confused with true values and there is a tendency for the heats of formation of fluorides to rise over the years, e.g. hydrogen fluoride. The criteria for calorimetric liquids include easy preparation, purification and recovery, a knowledge of chemistry in the media and reasonable physical properties at the standard temperature (25^{o}), e.g. viscosity, surface tension, vapour pressure and specific heat. Some physical properties are fixed by its reactivity, e.g. dipole moment and dielectric constant. Such requirements are satisfied by bromine trifluoride and fluorosulphuric acid.

The work described in this thesis establishes liquid phase fluorination methods of reaction calorimetry which are more versatile albeit less accurate than fluorine bomb calorimetry. The liquids used were fluorosulphuric acid and bromine trifluoride.

Bromine trifluoride can be made by direct combination of

the elements and can be purified by distillation, fractional freezing or zone refining. Because bromine trifluoride is the most reactive species in a bromine-bromine trifluoride solution, exceptional purity was not required and the trifluoride was purified by fractional distillation. It is highly reactive, most of the reactions giving quantitative yields, and the excess reagent is easily recovered. It is very similar in certain respects to water since it is liquid over approximately the same temperature range (8.77 to 125.75°) and ionic reactions occur in its solution. Reactions involving bromine trifluoride have been extensively studied since the work performed by Emeléus and his school. There is a recent comprehensive review by Stein[9] on the physical and chemical properties of bromine trifluoride. Unlike fluorine bomb calorimetry, which is hazardous and requires expensive equipment (Purification of liquid fluorine to remove oxygen and the gas is handled under pressure), calorimetry involving bromine trifluoride is relatively cheap and easy to perform. Thus provided reasonable precautions are taken when handling the trifluoride there is no reason why, once established, it should not prove a versatile calorimetric reaction medium.

It should be extremely useful for example to determine the heats of formation of binary fluorides by direct fluorination of the elements. In addition it is also of interest in its own right because of the unusual solvent properties which have been utilized to prepare complex fluorides. Thermochemical measurements should help to elucidate the mechanism of these processes which are still in dispute.

Values reported for the heat of formation of bromine

trifluoride have been obtained

1) By combination of the elements[10]

2) From the equilibrium $3BrF \rightleftharpoons Br_2 + BrF_3$[11]

together with the dissociation of BrF.

However there are uncertainties in both these techniques and the values obtained are gas phase values. Thus a heat of formation of liquid bromine trifluoride at room temperature appropriate to the reaction conditions had first to be determined in a variety of reactions and the derived value was then used to determine unknown heats of formation.

The calorimetry apparatus is described in Chapter I. The heat of formation of bromine trifluoride was obtained by measuring the heats of the following reactions. The stoichiometry of each reaction had been established previously.

1) $Mo + 2BrF_3 = MoF_6 + Br_2$

2) $3KBr + 4BrF_3 = 3KBrF_4 + 2Br_2$

3) $2KIO_3 + 6BrF_3 = 2KBrF_4 + 2IF_5 + 3O_2 + 2Br_2$

4) $6K_2SO_4 + 10BrF_3 = 6KSO_3F + 6KBrF_4 + 3O_2 + 2Br_2$

5) $3K_2S_2O_8 + 2BrF_3 = 6KSO_3F + 3O_2 + Br_2$

The above reactions apart from 1) are comparatively mild, and are increasingly complex. This work is reported in Chapter IV and a reasonably consistent value for the heat of formation of bromine trifluoride was obtained.

The critical point concerning the use of bromine trifluoride as a feasible reaction solvent is the influence of higher and lower fluorides formed in the reactions. Thus BrF could form via 1)

(1) $Br_2 + BrF_3 \rightleftharpoons 3BrF$

since Br_2 must be released when BrF_3 acts as a fluorinating

agent. A disproportionation reaction (2) is also feasible but it must be influenced by (1) since BrF is common to both reactions.

(2) $BrF_3 \rightleftharpoons BrF_5 + BrF$

The equilibrium (1) was studied by measuring the heat of solution of bromine over a range of bromine-bromine trifluoride concentrations. It was found that a partly saturated solution of Br_2 in BrF_3 was most suitable for reaction calorimetry. Although a reasonably consistent value was obtained for the heat of formation of the Br_2/BrF_3 solution the value probably refers to mixture of Br_2, BrF, BrF_3 and possibly BrF_5. However as this mixture was used to determine the heats of formation of other fluorides a somewhat "fictitious" value for the heat of formation of BrF_3 is not a bar to its future use. It is most probable that the reactive species in the mixture is bromine trifluoride.

All unknown or suspect auxiliary heats of formation were redetermined, i.e. iodine pentafluoride, potassium fluorosulphate, potassium tetrafluorobromate, potassium iodate and potassium persulphate.

The heat of formation of iodine pentafluoride was obtained by measuring the heat of reaction,

$$IF_5 + 6KOH = KIO_3 + 5KF + 3H_2O ;$$

of potassium iodate by measuring

$$KIO_3 + 6HCl + 5KI = 6KCl + 3I_2 + 3H_2O ;$$

of potassium persulphate by the reaction

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2 .$$

The heat of formation of potassium fluorosulphate involved the heat of formation of fluorosulphuric acid. The latter

value has been reported twice before[12][13] but both methods had unacceptable errors so the value was redetermined by measuring the heat of the following reaction in fluorosulphuric acid.

$$HF + SO_3 = HSO_3F \quad \text{(Excess HF)}$$

The work on halogenosulphuric acids was extended to measure the heat of formation of chlorosulphuric acid via

$HCl + SO_3 = HSO_3Cl$ in chlorosulphuric acid, and

$HSO_3Cl + H_2O = H_2SO_4 + HCl$ in water.

Chlorosulphuric acid is a potential calorimetric medium for organic substances. The heats of formation obtained were combined with free energy functions to calculate possible dissociations of the acids. The theoretical values were compared with experimental observations and are reported in Chapter II.

Chapter III contains an account of reaction calorimetry with fluorosulphuric acid. The heat of formation of potassium fluorosulphate was obtained by measuring the following heats of reaction

1) $K(CH_3COO) + HSO_3F = KSO_3F + CH_3COOH$ in acetic acid.

2) $K_2SO_4 + 2HSO_3F = 2KSO_3F + H_2SO_4$)
$KF + HSO_3F = KSO_3F + HF$) in HSO_3F

Fluorosulphuric acid proved such a useful calorimetric liquid; liquid range (-89° to 164°); is easily prepared, purified and recovered; that reactions studied in it were extended. The heats of formation of potassium, sodium, cupric, nitrosonium and nitronium fluorosulphates were determined. The unknown heats of formation of nitrosonium hydrogen sulphate and disulphate were obtained by heats of reaction in alkaline hypochlorite

solution. The regularities in heats of formation between perchlorates, hydrogen sulphates and fluorosulphates of the same cation were correlated by heat cycles. The proximity of the values for hydrogen and fluoro-sulphates was an important empirical observation. Heats of protonation of water and organic bases in fluorosulphuric acid were measured and were approximately related to the degree of ionisation in that solvent. Values for the enthalpies of formation and free energies of other ionic fluorosulphates were estimated from heat cycles or by comparison with hydrogen sulphates. The stabilities of some unknown fluorosulphates were predicted.

In Chapter V ionic reactions in bromine trifluoride are described. The high specific conductance of bromine trifluoride 8×10^{-3} ohm^{-1} cm^{-1} at 25^{o} [14] was attributed to the following ionisation:

$$BrF_3 \rightleftharpoons BrF_2^+ + F^-$$

(the other alternative BrF_2^- and F^+ is not feasible energetically). The small F^- ion can then be assumed to solvate, $F^- + BrF_3 \longrightarrow BrF_4^-$

Overall $2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$

Emeléus and Sharpe[15] found that some chlorides, bromides and iodides were converted to simple fluorides by action of BrF_3 but potassium, barium and silver chlorides formed complex compounds. The adducts formed were $AgF.BrF_3$, $KF.BrF_3$ and $BaF_2.2BrF_3$. X-ray diffraction showed absence of simple fluorides or BrF_3. The 1:1 ratio of BrF_3: Metal for K and Ag, and 1:2 for Ba, indicated that salts were formed; the tetrafluorobromates (III) of the respective metals. Seigel[16][17] has confirmed the existence of the BrF_4^- ion in $KBrF_4$ by X-ray diffraction methods

and similar lattice dimensions are reported by Bouy.

In a similar experiment the adduct $SbF_5 \cdot BrF_3$ was formed which ionized in bromine trifluoride. SbF_5 is a non conductor and almost always goes into anions, hence $BrF_2^+SbF_6^-$. This was confirmed by conductiometric titration with $KBrF_4$ in BrF_3.

$$K^+BrF_4^- + BrF_2^+SbF_6^- = KSbF_6 + 2BrF_3$$

$SnF_4.2BrF_3$ has not been isolated and can only be observed in solution by titration with $KBrF_4$.

Recently the crystal structure of $BrF_2^+SbF_6^-$ has been examined by Edwards and Jones[18] who deduced that the molecular symmetry is consistent with weak fluorine bridging. There is a slightly distorted octahedral coordination of the antimony by fluorine atoms. The structure can be best considered as predominantly derived from the ionic formulation $BrF_2^+SbF_6^-$. The solid structure is likely to lead to the formation of BrF_2^+ and SbF_6^- ions when dissolved in liquid BrF_3 by breaking the weakest bridge bonds in agreement with conductivity data. A similar structure $ICl_2^+SbCl_6^-$ was obtained for ICl_3SbCl_5[19].

Emeléus and Woolf[20] using the terminology applied to other solvent systems such as water and ammonia, classify as "acids" those compounds which contain the cation BrF_2^+ and as "bases" those which contain the anion BrF_4^-.

Some stable acids and bases are listed below.

Acid	Base
BrF_2SbF_6	$NaBrF_4$
$(BrF_2)_2SnF_6$	$KBrF_4$
BrF_2BiF_6	$AgBrF_4$
BrF_2TaF_6	$RbBrF_4$
BrF_2NbF_6	$CsBrF_4$
$(BrF_2)_2PtF_6$	$Ba(BrF_4)_2$
$(BrF_2)_2PdF_6$	$NOBrF_4$

The dissolution of an acid or base in bromine trifluoride causes the conductivity to increase. Titrations have been carried out in which the end point, corresponding to neutralisation of an acid by a base, is indicated by a sharp minimum in conductivity. Titrations of BrF_2SbF_6 or $(BrF_2)_2SnF_6$ with $KBrF_4$ in bromine trifluoride would proceed as follows

$$BrF_2^+SbF_6^- + K^+BrF_4^- = KSbF_6 + 2BrF_3$$

$$(BrF_2)_2^+SnF_6^- + 2K^+BrF_4^- = K_2SnF_6 + 4BrF_3$$

To obtain the salt produced by neutralisation the excess solvent is evaporated off. Thus it is an extremely useful method for the synthesis of new compounds. A large number of complex fluorides obtained from neutralisation reactions in bromine trifluoride are listed by Stein[9].

Heats of neutralisation of strong acids and strong bases in aqueous solution are reasonably constant. Similarly there should be a reasonably consistent value for the heats of neutralisation of strong acids and bases in bromine trifluoride. This would also give a value for the neutralisation heat of

$$BrF_2^+ + BrF_4^- = 2BrF_3$$

From these heats of neutralisation the heats of formation of a

large number of ternary fluorides could easily be obtained.

The heats of formation of a number of acids and bases in bromine trifluoride were measured. The compounds dissolved in bromine trifluoride to form acid solutions were antimonic, stannic and tantalic fluorides and sulphur trioxide, although there is some doubt as to the species formed when sulphur trioxide is dissolved.

The heats of reaction of the following compounds in bromine trifluoride, forming bases, were measured; sodium, potassium and barium fluorides and silver bromide. The heat of solution of lithium fluoride was also measured. It has a low solubility and a low heat of reaction indicating that only a weak base was formed.

The heats of neutralisation of the following acids and bases in bromine trifluoride were measured.

Base	Acid	Complex
$KBrF_4$	BrF_2SbF_6	$KSbF_6$
$AgBrF_4$	BrF_6SbF_6	$AgSbF_6$
$Ba(BrF_4)_2$	$2BrF_2SbF_6$	$Ba(SbF_6)_2$
$NaBrF_4$	BrF_2SbF_6	$NaSbF_6$
$2KBrF_4$	$(BrF_2)_2SnF_6$	K_2SnF_6
$2NaBrF_4$	$(BrF_2)_2SnF_6$	Na_2SnF_6
$Ba(BrF_4)_2$	$(BrF_2)_2SnF_6$	$BaSnF_6$
$KBrF_4$	BrF_2TaF_6	$KTaF_6$
$KBrF_4$	$BrF_3.SO_3$	KSO_3F

Thus a series of values of the heat of ionisation:

$BrF_2^+ + BrF_4^- \rightleftharpoons 2BrF_3$ was obtained.

The heat of neutralisation was dependent upon the strength of the acid and base used, because with weak bases and acids solvolysis

occurs preventing complete reaction, low values being obtained. Once the heat of formation of the acid and base in bromine trifluoride is known the heat of formation of the complex formed by neutralisation can be predicted with reasonable accuracy from the heat of neutralisation.

In Chapter VI the possible applications of bromine trifluoride as a calorimetric reaction liquid are discussed. The heats of formation of antimony pentafluoride and stannic fluoride were obtained by reacting the metals with bromine trifluoride. The heat of formation of $SeOF_2$ was obtained by converting it to the hexafluoride with BrF_3. An interesting application was to determine the difference in the heats of formation of monoclinic and orthorhombic forms of stannous fluoride.

The heat of formation of arsenic trifluoride is reported in Appendix I.

The thesis is concluded with relevant equations collected in Appendix II and description of analytical methods in Appendix III.

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CHAPTER I

CALORIMETRIC TECHNIQUE

ADDENDUM

(i) $\pm$: mean deviation of results

(ii) sign convention:- (a) thermodynamic for heats of formation (i.e. negative); (b) thermochemical for heats of reaction (i.e. positive heat for an exothermal reaction).

(iii) the physical states in equations are the normal states of the compounds at $298^{o}K$ and 760 mm. Hg.

REACTION CALORIMETRY

Introduction

In principle, the change in enthalpy accompanying a chemical reaction can always be calculated from heat of formation data, for all the participating substances. For many reactions this data is not available. The determination of a single heat of combustion can be a tedious and time consuming task. In some reactions one or more of the participants may be too unstable for investigation by the combustion method. Also there are many combustion reactions which are difficult to complete and involve assumptions in the analysis. Hence there has been a recent expansion in reaction calorimetry, which embraces a much wider range of experimental conditions and reaction systems, and from which enthalpy changes can be determined.

It is impossible to design a universally useful reaction calorimeter to cover the variety of chemical reactions, in the same sense as a combustion bomb calorimeter is a standard reactor. However the principal factors which influenced the choice of calorimeter design are listed below.

1) The rate of the reaction.

Calorimetry was restricted to reactions that were complete within a few minutes for simplicity of calorimeter construction. Slow reactions present severe problems if accurate results are sought and either an adiabatic calorimeter has to be designed or extreme control of heat flux is required to extrapolate over long periods.

2) The magnitude of the heat effect.

This is normally determined by the scale of the calorimetric

apparatus and the heat capacity of the calorimeter. The magnitude of the heat evolved was controlled by varying the amounts of reactants used. However for violent reactions in bromine trifluoride a special "twin-cell" calorimeter of high water equivalent was designed. Reactions involving low energy processes, e.g. Heats of solution, were carried out in conventional calorimeters.

3) The temperature of the experiment.

All reaction calorimeters were designed for operation at 24° and stirred liquid-filled calorimeters were used.

4) The level of accuracy to be achieved.

High precision in calorimetry demands not only accuracy in calorimeter performance but also well defined states of reactants and products. Thus there is little point designing a calorimeter accurate to 0.1% if the stoichiometry of reaction under investigation can only be analysed to 1% accuracy. Often it is the reaction under investigation which is the limiting factor and many reactions are so contaminated by side reactions that they are quite unsuitable for calorimetric study. The reactions studied merited reasonable precision in the calorimetry and hence refinement was needed not only in calorimeter design but also in subsidiary equipment which included thermostats, timing devices and electrical calibration apparatus. The calorimeters were designed for moderate accuracy (0.1 to 0.5%). However the accuracy in heat measurement was determined by the calorimetric liquid or reactant. It was easier to obtain higher accuracy with water than with bromine trifluoride or fluorosulphuric acid. When the latter solvents were used the addition of any impurity (e.g. moisture or organic material) produced a

significant heat effect which was not encountered in aqueous reactions. The accuracy of the results was sometimes influenced by the reactant added, less accurate results being obtained when using either unstable or hygroscopic materials. The errors in measuring heats of reaction are discussed later.

5) The nature and the number of phases taking part in the reaction.

This affects the design of the ampoule holder and ampoule breaker. If gases are to be introduced a chimney has to be provided extending from the calorimetric liquid to above the level of the thermostat and this is a source of heat leakage.

6) The reactivity of the materials.

This was a very important consideration in view of the extreme reactivity of bromine trifluoride. Hence all apparatus for reaction calorimetry in bromine trifluoride was either made of nickel or nickel plated metal. The materials used for O-rings and other seals were polytrifluorochloroethylene (Kel-F) or polytetrafluoroethylene (Teflon). In view of the explosive reaction of BrF_3 with water the calorimeter used for mild reactions in BrF_3 was not completely immersed in the thermostat. The temperature of the lid was kept constant by pumping thermostat water through copper tubing soldered to the lid. This left the O-ring seal unexposed to water.

7) The pressure to be applied during the reaction.

Items (5) to (7) influence the design of the reaction vessel with respect to materials of construction, devices for introducing, stirring and mixing of reactants and whether the vessel is sealed or connected to the atmosphere.

The majority of reaction calorimeters that have been

designed are of the non-isothermal type in which the heat of chemical reaction causes a proportional change in the temperature of the calorimeter which is measured. Non-isothermal calorimeters are operated either with a constant temperature environment or under adiabatic conditions. The adiabatic method is preferable for the study of slow reactions, for fast reactions the constant-temperature-environment calorimeters have the advantage. As fast reactions were studied, constant temperature-environment-calorimeters were designed.

Constant-temperature-environment calorimeters.

The calorimeter is completely surrounded by a jacket of constant and uniform temperature, the essential purpose of which is to maintain the thermal head between the calorimeter and its surroundings.

Provided the thermal head does not exceed $3^{o}C$ the heat exchange between the calorimeter and surroundings follows Newton's Law, so that:

$$\frac{d\theta}{dt} = k\,(\theta_j - \theta)$$

where θ_j = jacket temperature, θ = calorimeter temperature and k = leakage modulus of that system. However heat transfer due to convection does not follow the above equation. Since it is very difficult to evaluate the thermal leakage during an experiment, other than from the starting point of Newton's Law, it is important to keep convective transfer as small as possible.

In a well designed calorimeter and jacket system the leakage modulus should be constant (within limits of c.2%) and should be as small as possible. The following points were observed when designing the calorimeters.

(1) The jacket walls were kept at uniform constant temperature throughout the experiment.

(2) The outer surface of the calorimeter and the inner surface of the jacket were highly polished to minimise heat transfer by radiation between them.

(3) The calorimeter liquid was well stirred to ensure uniformity of temperature and the stirring rate was kept constant to ensure a constant heat of stirring throughout the experiment.

(4) The calorimeter should preferably be completely sealed to prevent loss by evaporation during the experiment. With the nickel plated brass calorimeter (see later) this was impracticable, so the temperature of the jacket θ_j was chosen to always exceed the calorimeter temperature θ throughout the experiment. It was suggested by White[1] that errors are introduced if Newtonian rates change sign during an experiment.

(5) The air gap between the calorimeter and jacket should be evacuated to reduce conductive and convective transfer, however this was not possible with the nickel plated brass calorimeter. In practice it made little difference to calorimeter performance and satisfactory results were obtained when the recommended standard heats of reaction were measured. The main effect due to non-evacuation was the greater differences in leakage modulii during the experiment.

Summary of calorimeters and techniques used.

Three "constant-temperature-environment" calorimeters of medium accuracy were designed, assembled and tested.

(1) A modified version of a Dewar flask calorimeter (250 ml. capacity) described by Finch and Gardner[2]. This was used for reactions in water and acetic acid.

(2) A modified version, in nickel plated brass (200 ml. capacity), of the type described by Gerding, Leden and Sunner[3]. This was used for work involving halogenosulphuric acids and mild reactions of bromine trifluoride.

(3) A "twin-cell" calorimeter for violent reactions with bromine trifluoride. This consisted of two nickel cylinders connected via a needle valve. One cylinder contained bromine trifluoride which was metered into the reactant in the other cylinder by applying suction. The whole was immersed in carbon tetrachloride in a Dewar vessel (850 ml. capacity) in which all measurements were made.

The heat of chemical reaction was obtained by comparison with a known electrical heat imput. Current and potential measurements were made with respect to a standard ohm resistor and a precision potentiometer ($\pm$0.002%). Timing intervals were controlled by an electrical relay actuating a stop-watch (0.02 second interval). Temperature was measured by a thermistor bridge circuit balanced with a medium sensitivity galvanometer following a galvanometer preamplifier. Resistance changes corresponding to 0.0001^{o} intervals were meaning-fully measured. Electrical calibration was effected by passing current from a 12v. lead accumulator through a non-inductively wound heater.

The experimental cycle was approximately one hour. All resistance readings were converted to temperature by calibrating the thermistor against a Beckmann thermometer. The corrected temperature changes were obtained using the method described later and all results were calculated on a computer.

Calorimeters (1) and (2) and the technique adopted were tested with the recommended reactions. (a) Heat of solution

of KCl in 275 moles of H_2O (b) The heat of neutralisation of tris(hydroxymethyl)aminomethane with 0.1NHCl.

Description of Apparatus and Calorimeters.

Temperature Control.

Reaction calorimetry requires temperature control devices to maintain constant ambients in the calorimeter room and in the calorimeter jacket.

The temperature control of the calorimeter room was not controlled but was constant to within $\pm\frac{1}{4}^{o}C$ over the experimental period. The degree of control required of the constant-temperature-environment jacket is much more stringent and a constancy of at least $\pm 0.002^{o}$ over the experimental period was obtained using a toluene-mercury regulator and an electromagnetic relay.

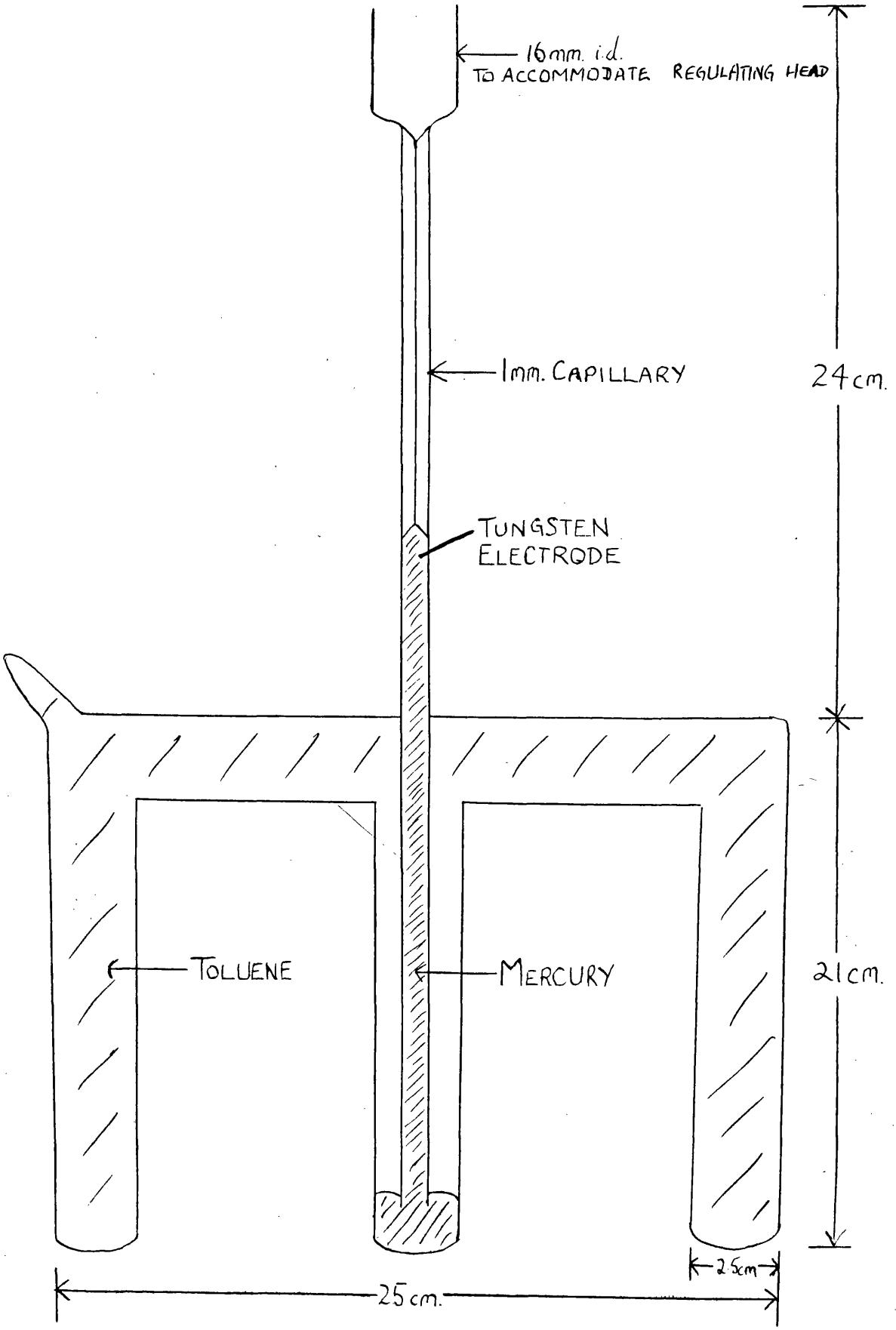
Control of Thermostat.

All calorimeters were immersed in a stirred water bath at 24^{o}. The water bath (65 litres capacity) was insulated by polystyrene sheets (1.5cm. thick) and heated by a kilowatt heater coupled with an autotransformer. The temperature control of the bath depends not only on the devices employed but on the positioning of the controller with respect to the stirrer and heater. This factor was discussed by Sturtevant[4] in relation to the prevention of instability of the control system revealed by oscillations in the bath temperature about the mean. An effective way of reducing lags below the oscillation point is to place the control so that it receives the liquid flowing away from the heater. A satisfactory system adopted was to stir the bath with a propeller stirrer in a cylindrical tube with a 45^{o}

baffle at the bottom directing the flow over the heater and the control device mounted to receive the stream delivered by the stirrer tube.

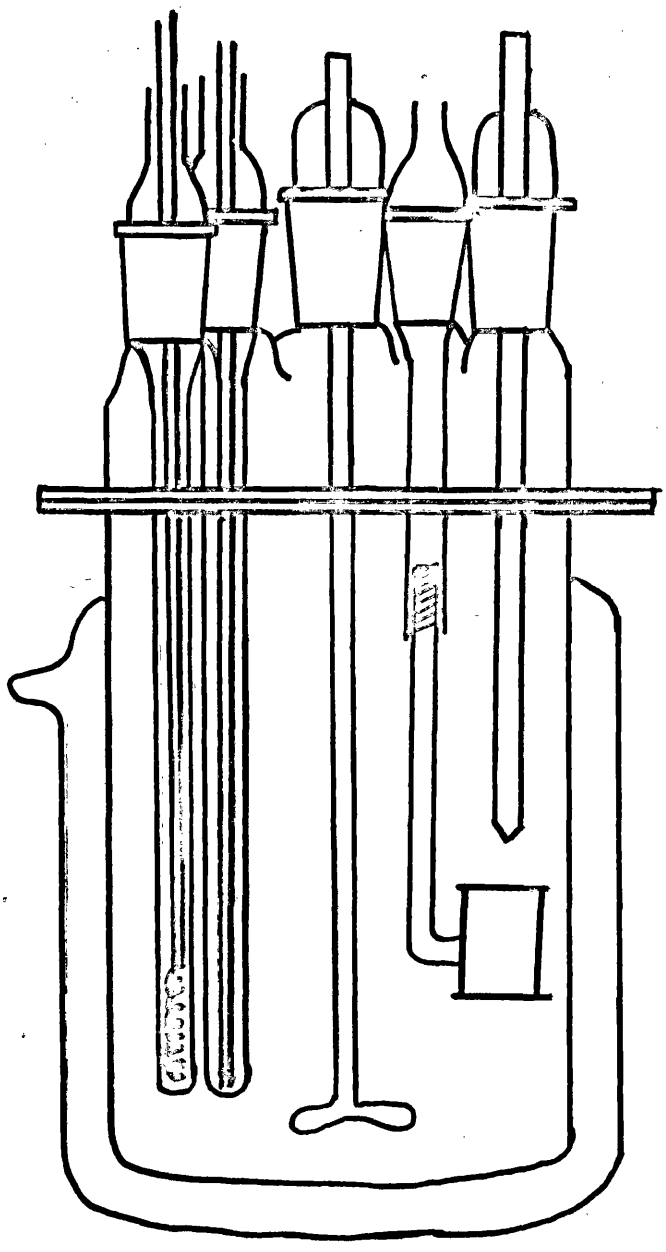
The temperature was controlled by a large toluene/mercury regulator (see Fig.1) with an electric equivalent of the Gouy oscillating head (Sunvic thermoregulator proportionating head type Tol 3C) and valve relay. The sensitivity of the regulator was increased by filling it with toluene and a minimum of mercury as the electrical contact material. The lag on the regulator was decreased by increasing the surface to volume ratio. The fouling of the mercury surface in the capillary was largely eliminated by minimizing the make or break current with the relay. In the proportionating head the contact is attached to a bimetal strip. When the contact is made it turns off the bath heater and bimetal heater. The bimetal then cools, contracts, and raises the contact out of the mercury to switch on the heater current again. Conversely a rising mercury column delays the withdrawal of the contact because the bimetal is kept on longer. The net effect is to damp down the temperature oscillation by a factor of at least ten.

The toluene was purified to remove any sulphur compounds which would foul the mercury. Toluene was stirred with concentrated H_2SO_4. The lower acid layer was removed and the process repeated twice. The toluene was washed twice with 10% Na_2CO_3 and finally with water then dried over anhydrous calcium chloride. Toluene was filtered and distilled through an efficient column collecting the fraction boiling at 110.5° at 760mm.



TOLUENE/MERCURY REGULATOR

Fig. 1.



GLASS DEWAR-VESSEL CALORIMETER

Fig. 2.

Calorimeters.

a) Glass Dewar-vessel Calorimeter[2]. (See Fig.2)

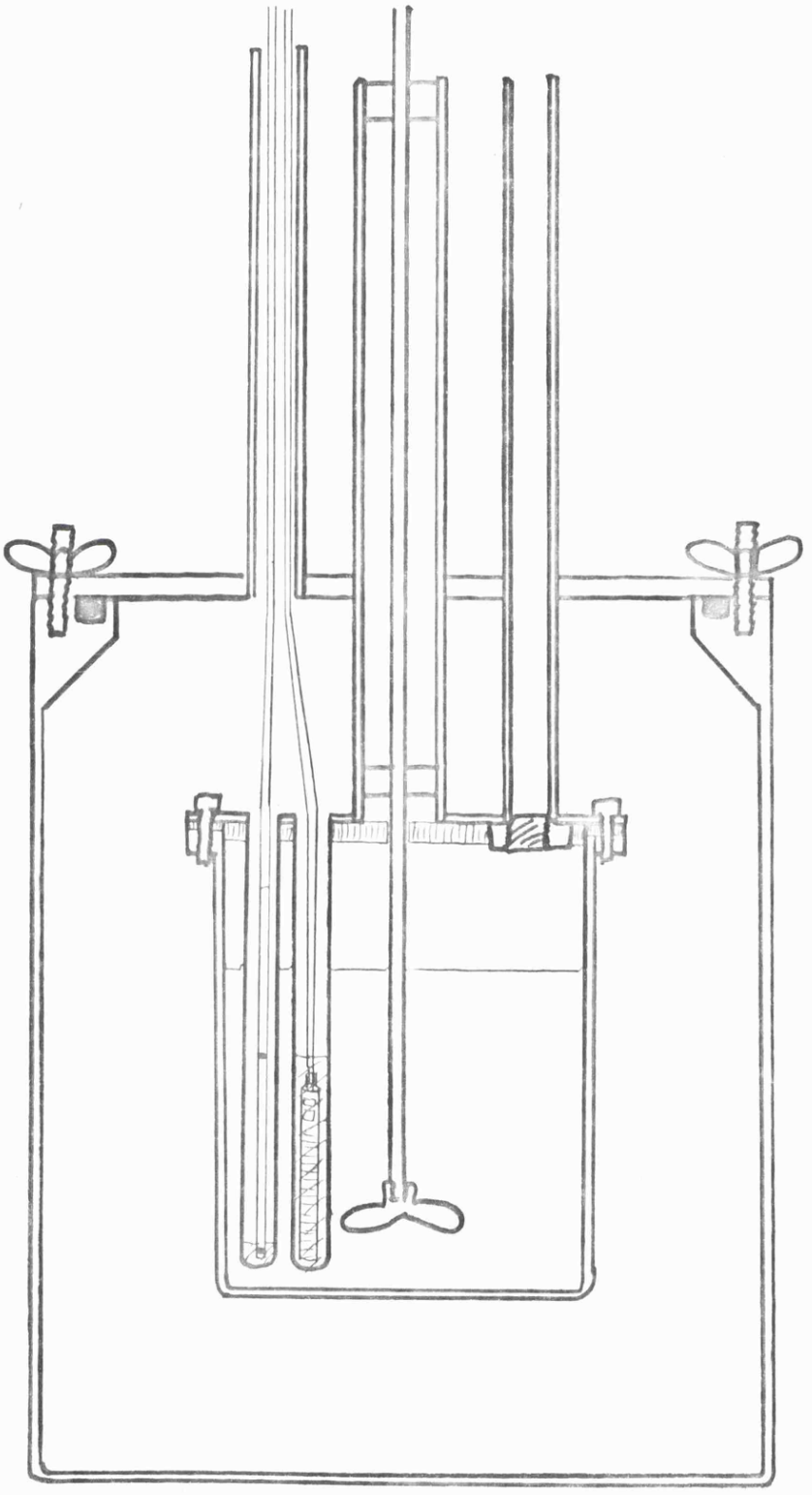
All heats of reaction in water or acetic acid were measured in this calorimeter. The advantage of glass Dewar-vessels for calorimeter construction is that they are inexpensive and readily replacable.

A Dewar type vessel (250 ml. capacity) was fitted with flanged joints which were well greased to keep the container liquid tight. The lid was permanently clamped to the calorimeter body. The vessel was immersed in the thermostat so that the water level covered the base of the necks on the lids. Five ground glass cones were fitted to the lid. The central B14 cone accommodated the stirrer and two other B14 pockets carried the thermistor (for temperature measurement) and heater (for electrical calibration). The final two carried the ampoule holder and ampoule breaker. All inner fitments were made of glass.

This calorimeter cannot be expected to give results of high precision but it is calorimetrically reliable in operation within error limits of about $\pm 0.5\%$. A recent study by Sunner and Wadsö on the efficiency of Dewar-vessel calorimeters showed that the main disadvantage was the very long time required to reach thermal equilibrium.

b) Nickel plated brass calorimeter. (See Fig.3)

This calorimeter was used for mild reactions in bromine trifluoride and reactions with fluoro- and chloro-sulphuric acids. The calorimeter consisted of an outer chromium plated brass can with a nickel plated brass lid. Two alternative inner cans also nickel plated were mated to an inner nickel plated brass lid.



NICKEL PLATED BRASS CALORIMETER

Fig. 3.

One was used for liquid reactants and the other for solids. The inner calorimeter vessel used for the introduction of solids under calorimetric liquids was fitted with a blade which was silver soldered centrally to the base of the can. This knife was used to rupture aluminium or Teflon foils used to hold solids in the nickel holder (see Fig.6). The inner cylinder used to introduce liquids consisted of a nickel holder for glass ampoules which was screwed to the centre of the base (see Fig.6). The amount of calorimetric liquid was from 100 to 130ml. All measurements were made in the inner can. The two lids were permanently linked by means of two thin walled stainless steel tubes. One carried the central propeller made of nickel tube. The use of tubing cut down heat loss by conduction along the shaft. The second was used for the introduction of gases into the inner can. The inner lid held two nickel plated stainless steel tubes one of which carried the heater and the other a thermistor. A Neoprene O-ring seal between the outer lid and can gave a leakproof enclosure. All connections between the interior of the system and surroundings were carried through metal chimneys protruding above the level of the thermostat water. The calorimeter was not evacuated.

A number of heat shields were tested but rejected as unnecessary. Heating runs were carried out with the following arrangements:

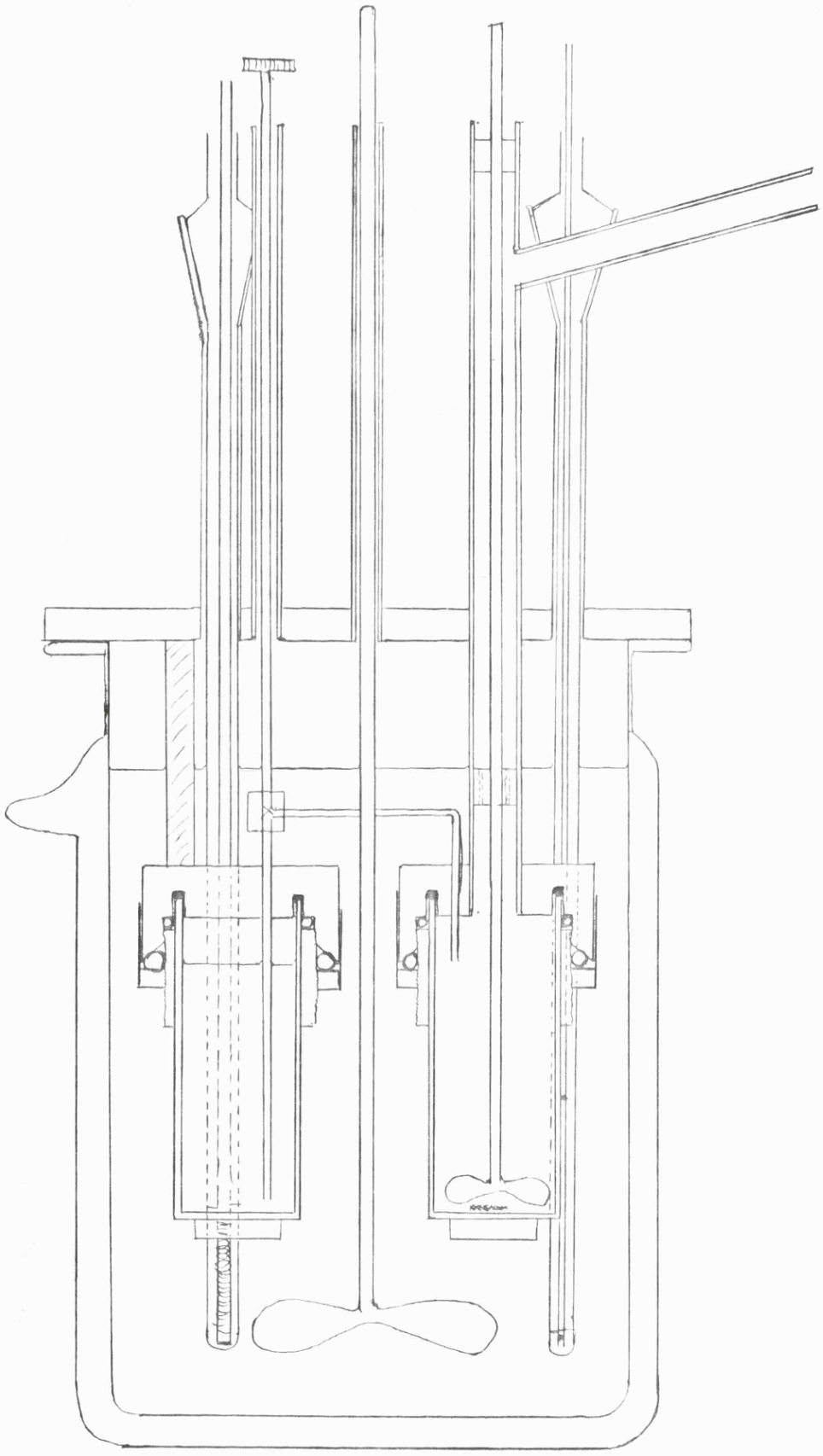
(a) No heat shield.

(b) Chrome plated brass (650g)

(c) Nickel foil (68g)

(d) Aluminium foil (4g)

The most consistent results were obtained without a heat shield.



"TWIN-CELL" CALORIMETER

Fig. 4.

Sunner and Wadsö[4] after studying a series of calorimeters, concluded that any system constructed with an intermediate boundary with respect to its surroundings tended to equilibrate slowly. Thus an insulating layer between calorimeter and surroundings introduces an appreciable time lag.

Modifications of the calorimeter for mild reactions in bromine trifluoride.

Due to the violence of the reaction of BrF_3 with water and organic materials the calorimeter was (a) not completely immersed because it was not absolutely possible to guarantee that leakage would never occur and (b) the rubber O-ring was replaced by a Teflon O-ring. The outer can was immersed in the thermostat to just below the level of this O-ring and the temperature of the lid was kept constant by pumping water through tubing on a brass plate which was in screwed contact with the outer lid. A Teflon washer was fitted between the inner lid and inner can to prevent leakage of the trifluoride.

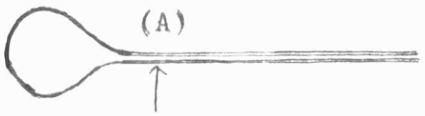
c) "Twin-cell" calorimeter for violent reactions with BrF_3. (See Fig. 4)

It consists of two cylindrical nickel chambers (25 ml. capacity) connected via stainless steel tubing and a Hone needle valve. One cell contained bromine trifluoride which was transferred to the other nickel cylinder, containing the solid reactant, by opening the valve and applying suction. If necessary a series of baffles and a stirrer were fitted in the receiver. The nickel lids of the twin cells were permanently attached to the brass lid, one by a nickel stirrer guide, and the other by a nickel tube. In one cell 3 mm. diameter stainless steel tubing reached to the bottom of the cylinder. The two cylinders were fitted with threaded brass rings on the

outside. The top of each cylinder was fitted with a Kel-F washer which was forced into a recess in the nickel lid by screwing up the cylinder. In addition the cylinders were made externally liquid-tight by rubber O-rings which fitted into tapers on the nickel lids and were fastened by brass collars fitted to the threaded brass rings mentioned above. The neoprene O-rings swell in carbon tetrachloride which helps to tighten the seal. The brass collar was fitted with flats to tighten up the rubber O-ring.

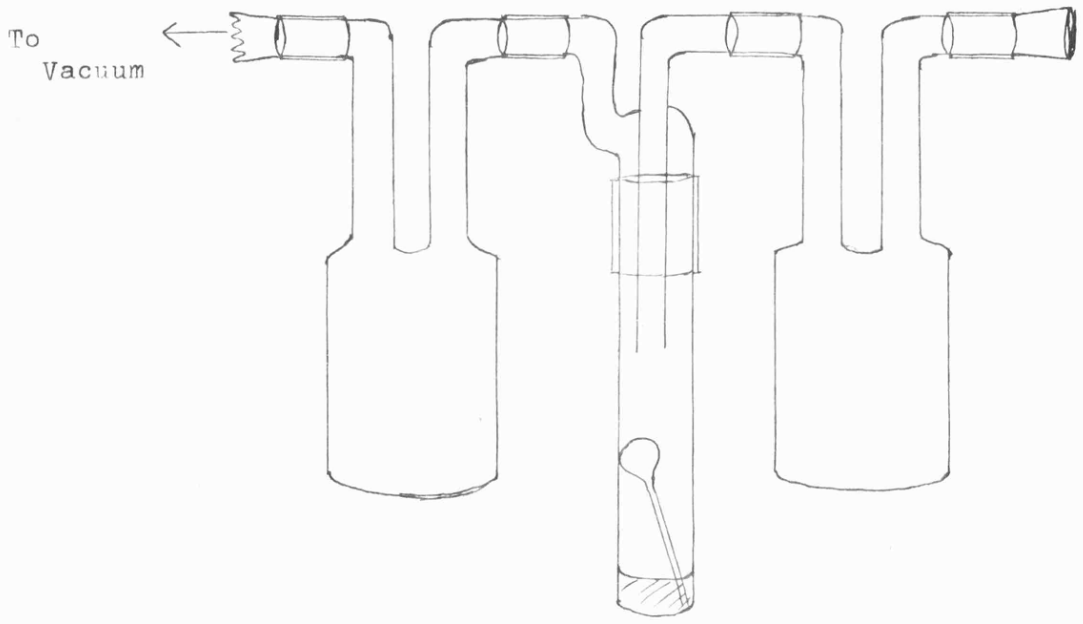
The metal assembly was immersed in 850 ml. of carbon tetrachloride, in which all measurements were made. Carbon tetrachloride was used because its reaction with BrF_3 to produce chloro-fluoro-carbons is comparatively mild. The carbon tetrachloride was held in a Dewar type vessel fitted with a well greased flange which mated with the flat brass plate making a liquid-tight enclosure. The brass plate was fitted with five chimneys. Two were 6 mm. bore copper tubing which carried a central glass stirrer and an extension of the screw control for the valve through which the BrF_3 was transferred. Two other chimneys were glass B14 sockets which carried the detachable heater and thermistor pockets. The remaining chimney was a nickel guide tube which accommodated a nickel tube stirrer to the nickel reaction cylinder. The stirrer hole was blocked off when suction was applied to transfer the liquid. The stirrer guide was fitted with a 6 mm. bore side-arm connected to a copper tube containing sodium fluoride pellets, suction being applied to the far side of the sodium fluoride tube. Sodium fluoride was used to prevent vapours from the bromine-bromine trifluoride solution contaminating the pump. When bromine

THIN-WALLED GLASS AMPOULE



Ampoule sealed at (A) in a flame

APPARATUS TO FILL AMPOULES ON THE VACUUM LINE



APPARATUS TO FILL AMPOULES IN A TUBE FITTED WITH A TWO-WAY TAP

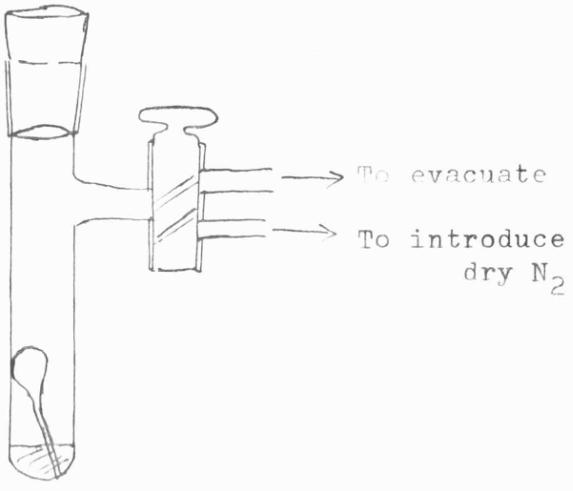


Fig. 5.

trifluoride had been transferred the sodium fluoride tube was removed and the exit tube stoppered to prevent entry of atmospheric moisture.

Pressure transfer was not used because:

a) It was hazardous and difficult to pressurize the nickel cylinder before assembly of the calorimeter.

b) To apply pressure to the cylinder, when the calorimeter had been assembled, would require an extra chimney.

Introduction of Reactants

(a) In Dewar vessel calorimeter.

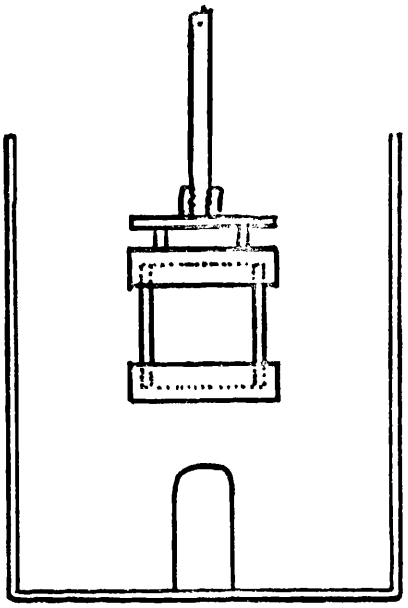
Solids were introduced in a glass tube (15 mm. diameter, 25 mm. long) sealed with thin glass cover slips at each end using "picien" wax. Liquids were sealed in thin-walled glass ampoules (see Fig.5) which were secured in the holder with "picien" wax. The uniformity of the glass ampoules used was checked by the weight. To fill, the bulbs were (a) evacuated (either on the vacuum line (see Fig.5) or using a stoppered glass tube fitted with a two-way tap), (b) allowed to refill under a stream of dry nitrogen and (c) sealed in a flame. Solid and liquid holders were immersed under the liquid in the calorimeter and broken by a glass spike. Gases were introduced through a tube fitted to a B14 cone in place of the normal holder and breaker.

(b) Nickel plated brass calorimeter. (See Fig.6)

Liquids were again introduced in thin-walled glass ampoules. The ampoules were secured in a nickel ampoule holder screwed to the base of the inner can and broken by a spike incorporated in the central stirrer. The windows in the nickel ampoule holder ensured complete mixing after the ampoule was broken. The

INTRODUCTION OF REACTANTS IN THE NICKEL PLATED BRASS CALORIMETER

Solids



Liquids

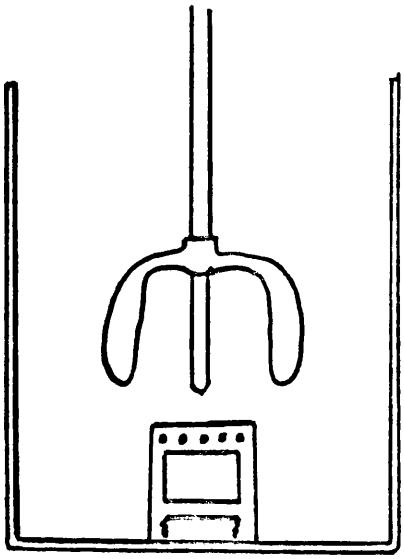


Fig. 6.

ampoule was held in place by nickel wire through holes at the top of the holder. Solids were sealed in a nickel holder, 15 mm. long and 15 mm. diameter. The holder was made liquid tight by two threaded annular caps which compressed foil on to the threaded nickel cylinder. Aluminium foil was normally used to seal the solid holder but Teflon foil was used for reactions in BrF_3. Zinc or nickel foil could also be used but thin gauge material was not readily obtained. The nickel holder was fitted with three nickel stirrer blades and the whole attached to the central stirrer. The foils were ruptured by thrusting the holder on to the nickel blade soldered to the base of the inner can.

Gases were introduced through the side arm as shown in the diagram.

(c) "Twin-cell" calorimeter.

The reactants were mixed by transferring BrF_3, by suction, from one cell into the other containing the solid reactant.

Stirrer

The stirrer was operated at 250 to 400 r.p.m. the speed being kept constant by a voltage stabiliser transformer (Type VST 120 Astralux Dynamic Ltd.) driving a Citenco variable speed motor. The voltage stabiliser was used to keep fluctuations in mains imput to $\pm$ 1%. It is essential to maintain a constant rate of stirring throughout the experiment to obtain accurate results. The stirrer speed had little effect on the measured heat of reaction provided it was sufficiently fast and did not cause excessive splashing.

Temperature Measurement

The commonly used temperature measuring instruments are:

a) Mercury-in-glass thermometers. The function measured is

the expansion of mercury. It has the advantage of direct reading and is relatively inexpensive. However, there are many disadvantages, it can only read to 0.002° and changes in bulb volume; effects of pressure; exposure of stem and irregular movement of meniscus all produce errors. Also there is a considerable time-lag.

b) Platinum resistance thermometers. The function measured is resistance. It is both very accurate and reproducible. The main disadvantage is the expense of the thermometer and resistance bridge.

c) Thermocouples. The e.m.f. generated by a thermocouple is a function of the difference in temperature between the two probes. The e.m.f. developed is usually small and hence multijunctioned couples needed.

d) Thermistors. The function measured is resistance. This was used in the calorimetric apparatus as described below.

Thermistors are made by sintering mixtures of metallic oxides - the oxides of Mn, Fe, Co, Ni and Zn being commonly used. A bead type thermistor was used consisting of two taut parallel Pt/Ir wires (c0.00025cm. diameter) bridged by a sintered oxide bead. The bead was protected with a thin sheath of glass, the two short tie-wires were fastened to thicker wires and the element sealed in a glass tube.

The most striking characteristic of the thermistor is its very high negative coefficient of resistance. The 1500 Ω resistance of the thermistor at 24° dropped by about 60 Ω for a 1° rise in temperature. The resistance of the thermistor (Stantel F23, 2,000 ohm nominal at 20°C) was measured with a conventional DC-Wheatstone bridge circuit with a light spot galvanometer of medium sensitivity (Pye 7901/S; 15mm./μA) allied

with a Pye preamplifier galvanometer (Cat. No. 11330). The overall sensitivity was about 2,000mm./μA. Using this apparatus resistance changes corresponding to 0.0001^{o}C intervals were meaningfully calculated. The listed response time of the thermistor was 5 seconds, but the actual response time depends upon the environment of the thermistor.

In using a thermistor for temperature measurement it was necessary to take the following precautions to ensure reproducible behaviour.

(i) The electrical dissipation in the thermistor was kept well below the manufacturers limit of c10mW. In practice about 1mW. was used. The thermistor current was kept reasonably constant.

(ii) Thermistors are sensitive to light and pressure fluxes and have been used in flow meters. Hence they were shielded and firmly mounted in a thermistor pocket with the tip immersed in silicone oil.

(iii) In calculating the corrected temperature (ΔT) the approximation that $\Delta T \propto \Delta R$ or $\log R_{i/R_f}$ where R_i and R_f are the initial and final resistances was not used because it is inaccurate except when employed for near identical R_i's and R_f's. Each resistance was directly converted to temperature by first calibrating the thermistor against a Beckmann thermometer (Range 5^{o}). The most used relationship between temperature and resistance was adopted.

$$R = A_e^{B/T}$$

R - resistance, T - temperature in ^{o}K, A and B are constants dependent on the particular thermistor.

Other relationships between resistance (R) and temperature (T) are:

a) $$\log R = A + \frac{B}{T+\theta}$$

Where A, B and θ are constants

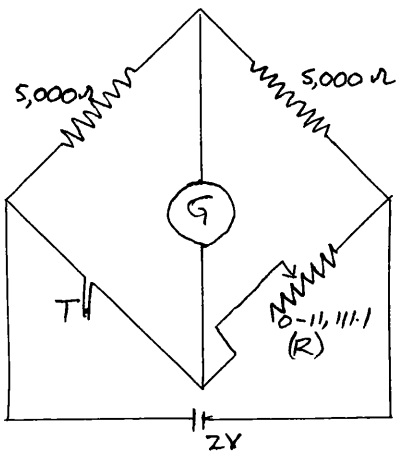
b) $$R_T = R_o \exp. \beta\left(\frac{1}{T} - \frac{1}{T_o}\right)$$

R_T - Thermistor resistance at T^oK

R_o - Thermistor resistance at $T_o{}^oK$

β - constant.

From the linear plot of log R vs. $^1/_T$ the two constants A and B were obtained. The absolute temperature on the Beckmann scale is not important as long as the scale is linear and reaction heats are directly compared with electrical power over the linear range.



G:- Galvanometer and preamplifier.

T:- Thermistor immersed in silicone oil.

R:- Precision resistance box.

The errors introduced by not converting all resistance readings to temperature are described by Wadsö[6]. For calorimetric investigations of moderate and even high accuracy the thermistor presents an attractive proposition. It is small in bulk, rapid in response, very sensitive and does not require

expensive auxiliary instruments. Its disadvantages are that temperatures are not absolute to within the accuracy it is capable of measuring and that long term stability is not perfect. The drift of thermistor resistance with time is not important because chemical and electrical heats are measured one after the other. The absolute temperature of the thermistor was obtained by calibration against a standard thermometer.

Electrical Calibration System.

Heater[7]

The heat was made from 0.15 mm. insulated manganin wire (resistance 25 ohms/metre) wound non-inductively on a brass former. The heater resistance was 27 ohms. The resistance wire was secured with an epoxy resin (Araldite), cured in the cold. The wire was soldered to 1 mm. enamelled copper wire leads which were introduced to the heater through a porcelain holder. Thin wires were used to reduce heat loss by conduction as discussed by White[1]. Holes were pierced in the top of the core to allow circulation of silicone oil in which the heater was immersed. The heater was fitted with separate current and potential leads.

Calibration of reaction calorimeter.

The calorimeter was calibrated by the substitution method in which one measures the amount of electrical energy needed to duplicate the thermal effect produced by the process under investigation. Hence the calorimetric investigation of a reaction consists of two parts in which one records

(a) The time-temperature curve of the calorimeter contents during an experiment in which a measured amount of the chemical reaction takes place.

(b) The time-temperature curves during an experiment in which a measured amount of electrical energy is expended as heat within the calorimeter before and after (a).

In the event that the curves recorded in the two types of experiments (a) and (b) were identical, one would equate the unknown chemical energy liberated in (a) to the known electrical energy expended in (b).

In practice it is not possible or even necessary to exactly duplicate the curve from (a) in experiment (b). Nevertheless it is always desirable to maintain a close similarity between the two types of experiment, since when duplication is exact there is a cancellation of certain errors common to both experiments. Thus if a chemical process were to produce a temperature rise ΔT in x minutes in the calorimeter one should adjust the electrical energy imput in the calibration experiment to imitate the form of temperature rise in the same time interval. The electrical calibration was carried out before and after the chemical reaction and the mean of calibration runs used to average out specific heat changes.

Electrical Calibration.

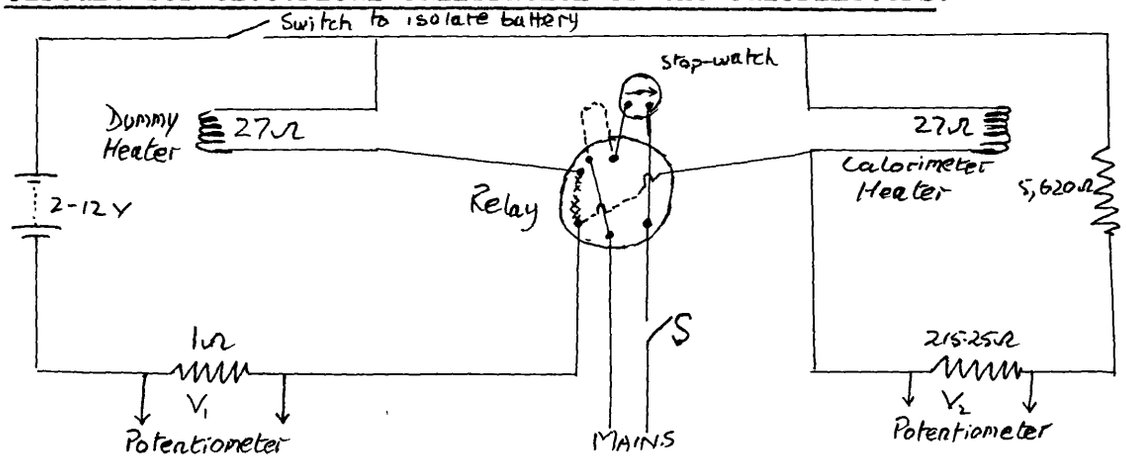
Part of the voltage from a 12v heavy duty storage battery was applied to a dummy heater (27 ohms) for at least 1 hour before each calibration experiment to ensure equilibrium conditions in the electrical circuit. The calibration time was measured using an electrical contact stop-watch (Jacquet 309e), 0.02 second interval operated from the dummy heater reversing switch. The difference between the measured and true calibration time was obtained by comparison with a quartz crystal timer (Venner multisecond stopclock type TSA 3314). In all experiments the

error in timing was not greater than 0.01%. The stop watch was used over the most accurate period, 5 to 15 minutes from the watch being fully wound. Current and potential measurements were made with respect to a standard 1 ohm (±0.002%) resistor on a Pye Precision Vernier Potentiometer (0.002%) Cat. No. 7568). The potentiometer circuit was balanced with a Pye galvanometer (Type 7903/S 84mm./μA). The potentiometer was standardised against a Weston standard cell, temperature compensated by means of a built in resistor. For experiments a substandard 1 ohm resistor (±0.2%) was used in the circuit which was calibrated against the standard ohm resistor by direct replacement in the circuit. All connections were made using solder with low thermal e.m.f., 0.31 μv./°C cf. 3.2 μv./°C for normal solder.

Units of energy.

The value for the calorie has been arbitrarily fixed in terms of joules. At present there are two values for the calorie, the International Table (IT) and thermochemical. Any confusion that may arise between the two could be resolved by all data being reported in joules, the actual unit of measurement. Because the majority of thermochemical data is reported in thermochemical calories, this unit is used in this thesis, 1 calorie = 4.184 joules.

Circuit for electrical calibration of the calorimeters.

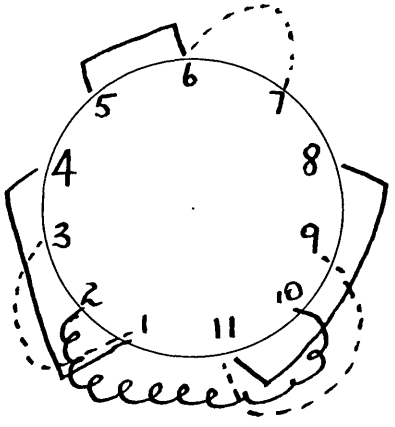


S - Switch to relay, when relay open ××××× connected.

closed ---- is connected.

The Relay normally passes current through the dummy heater (similar resistance to calorimeter heater). On energising, it switches on the calorimeter heater and stop watch. All connections were clean and firmly made. All resistances used in the circuit were checked on the Wheatstone bridge circuit.

Relay used for calibration of calorimeters.



——— Joined when relay open

- - - - - - Joined when relay closed.

eeee MAINS

1.	12v	6.	To No.2
2.	Mains	7.	Stopwatch
3.	Not used	8.	Not used
4.	Dummy heater	9.	Calorimeter heater
5.	Not used	10.	Mains.
		11.	To No.1.

Experimental Procedure.

In the Dewar type calorimeters all measurements were made at approximately 24° but in the non-evacuated nickel plated brass calorimeter a temperature difference was maintained between the calorimeter and thermostat. First a calibration heating run was performed followed by the chemical reaction and finally another calibration run. Linear rates of heating or cooling due to heat exchange between the calorimeter and surroundings and

effect of stirring, preceded and followed each reaction heat imput. The time to reach equilibrium conditions after heat imput was approximately ten minutes. In the Dewar type calorimeter the rates of Newtonian cooling were quite small and virtually constant. With the nickel plated brass calorimeter the rates were larger and slightly more variable. The overall temperature rise was 1.5 to 2° and the experimental period was approximately 40 to 60 minutes.

Heats of mixing of reactants.

In calorimeters (a) and (b) the chemical reaction period was started by breaking an ampoule and mixing the solid or liquid contents with the calorimetric liquid.

Many authors have pointed out that the breaking of a bulb may give rise to one or more small heat effects. The main sources of such heat effects are as follows:-

a) The heat of stirring is dependent upon the environmental situation. If the bulb is situated close to the stirrer the heat generated by friction between the liquid and the unbroken bulb might be significantly different from that generated between the liquid and the remnants of the broken bulb. Also glass fragments give rise to an additional heat of stirring. When using aluminium or Teflon foil there is a slight alteration to the heat of stirring due to the effect of the ruptured foil on the stirring conditions.

b) The heat of rupture of a bulb depends on the mechanical properties of the glass, a variable quantity in any event, wall thickness, internal strain etc. With rather large and rigid ampoules the heat of breaking may be considerable. Glass ampoules used were blown from the smallest amount of Pyrex glass

required to form a rigid ampoule of the required size. Glass ampoules were made without a mould and to keep the variance in thickness and strain to a minimum, only ampoules of a certain size and shape were selected, (0.1 - 0.2g. glass for a bulb 7-12 mm. diameter).

c) The heat of wetting of the inner surface of the glass bulb is usually a negligible quantity being only of interest in micro calorimetric measurements.

d) A considerable effect on the heat of mixing may arise from attack on the ampoules or foil by the calorimetric liquid. This is important when using fluorosulphuric acid solutions and especially bromine trifluoride. (See later)

Possible sources of error in experimental procedures.

Apparatus.

a) The timing of the calibration runs was in error by no greater than 0.010%.

b) The accuracy of the current and voltage readings was 0.005 to 0.01%.

Errors in measuring resistors used in the circuit were extremely small and can be neglected.

Error in techniques used.

a) Breaking of ampoules.

The heats of breaking of all ampoules were determined but it was difficult to standardise the assembly and breaking of ampoules when performed manually. Although the heat of breaking of glass ampoules were reasonably consistent (see later) the variability remains a source of error. Another error may be due to non-uniformity of ampoule assembly and breaking when using aluminium and Teflon foil. For example the strength of the latter foil

varies with orientation. Variable heats of stirring in the nickel plated brass calorimeter after the ampoule was broken may have been obtained due to:

1) Difficulty in returning the stirrer to its original position as the solid holder was detached from the central stirrer while the foil was broken.

2) The ruptured foil (Aluminium or Teflon) after the solid was introduced.

3) Attack of BrF_3 on Teflon. This extra heat was detected from the incorrect heats of stirring when the heat of breaking was measured. When the foil was ruptured, the pretreated foil was stretched exposing new surface to attack.

b) Error in having ampoules only partly filled with liquids.

1) Evaporation of calorimetric liquid.

Often the ampoule in reaction calorimetry is not completely filled but contains a partial pressure of air which will pass through the calorimetric liquid and become saturated with its vapour. This effect is small and can be corrected by breaking empty ampoules.

Heat effect: Assume 0.5 ml. of air in bulb above liquid to cause evaporation of the calorimetric liquid. If the liquid is water, vapour pressure at 25° is 25 mm. Hg. and the heat of evaporation is 10.5 kcal./mole. The molar volume for a gas at 25° is about 24.4 litres.

$$\text{The heat effect} = \frac{0.5 \times 10^{-3} \times 24 \times 10{,}500}{24.4 \times 760} = 0.007 \text{ cal.}$$

2) Partial evaporation of ampoule content.

When the ampoule is incompletely filled part of the ampoule content is in the vapour state. This is usually small enough to

be neglected. However if the liquid had a high vapour pressure at room temperature, the bulbs were virtually completely filled to avoid this error due to partial evaporation.

Heat effect due to partial evaporation: If the bulb (1 ml.) is half filled with methanol (vapour pressure at 25° 125 mm. Hg. and heat of vaporization 8.9 kcal./mole).

Heat of vaporisation = $\frac{0.5 \times 10^{-3} \times 125 \times 8,900}{24.4 \times 760}$ = 0.03 cal.

These heat effects (1) and (2) are small enough to be neglected.

c) Condensation effect as a result of solution of the ampoule content.

When a substance is dissolved in a solvent the vapour pressure of the solvent will decrease. However it has been reported by Wadsö[6] that condensation effects from this origin are small and can usually be neglected.

d) Gas evolution in the reaction.

When in a reaction a gas is evolved and allowed to escape it will leave the system partly or fully saturated with the vapour of the calorimetric liquid. The corresponding heat effect is often substantial and may rarely be neglected. Oxygen was evolved in reactions with Br_2/BrF_3 solutions and the effect on the measured heat of reaction has to be determined.

The heat of vaporization of Br_2 at 25° = 7.6 kcal/mole.

The heat of vaporization of BrF_3 at 25° = 10.5 kcal/mole.

Vapour pressure of Br_2 at 25° = 213 mm. Hg.

Vapour pressure of BrF_3 at 25° = 7.64 mm. Hg.

A very approximate heat correction per mole of oxygen evolved may be calculated to be :-

for BrF_3 = $\frac{76 \times 10,500}{760}$ = 0.105 kcal .)
) 2.24 kcal , assuming ideality
for Br_2 = $\frac{213 \times 7,600}{760}$ = 2.13 kcal .)

It is difficult to calculate an accurate value for this correction because the vapour species, and their heats of vaporization have not been fully characterized. A correction has been determined experimentally by passage of a known volume of oxygen through the solvent assuming that the rate of passage does not influence the correction appreciably. This is one of the main errors in reaction calorimetry in bromine trifluoride when oxygen is evolved. The heat due to gas evolution was measured and was 2.52 $\pm$0.13 kcal./mole.

e) Partial vaporization of volatile reaction components.

A volatile reactant or reaction product will to some extent evaporate into the gaseous space above the calorimetric liquid.

f) Temperature dependence of enthalpy value.

An enthalpy value is temperature dependent and for maximum accuracy corrections have to be applied to obtain an enthalpy value at exactly 298.2°K. However this work was not sufficiently precise to warrant corrections over the 1-2° interval involved.

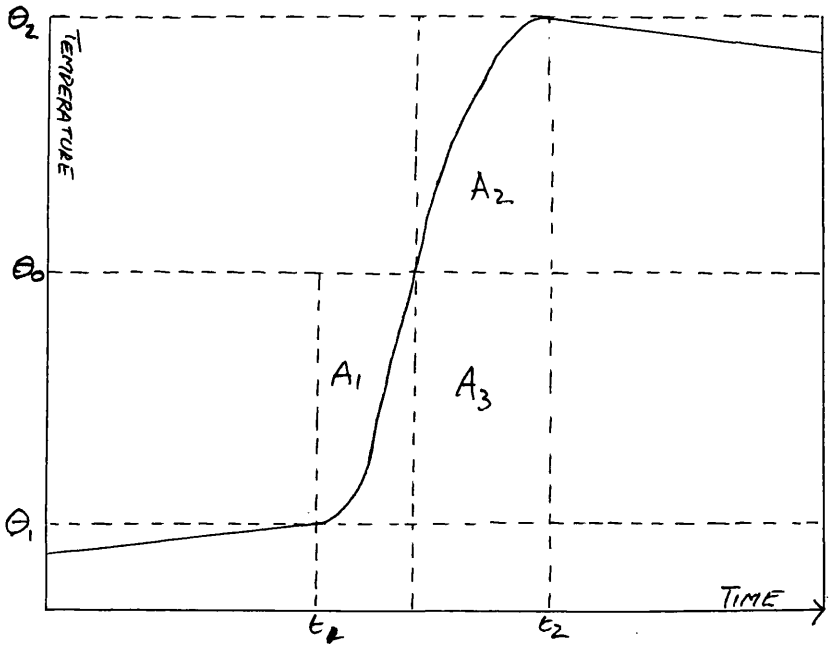
g) Weight correction.

Correction of weighings in air to those in vacuo was not necessary as it only affects the fifth place in weighing.

Calculation of results.

Calculation of corrected temperature rise[8].

The corrected temperature rise was evaluated making direct use of Newton's law, that the heat flux was proportional to the temperature head.



t_1 - start of the reaction, end of the preliminary period of Newtonian heating or cooling.

θ_1 - Temperature at start of reaction.

t_2 - Time at beginning of Newtonian cooling period.

θ_o - Temperature of surroundings.

θ^1 - Mean of consecutive temperature readings in reaction period.

Z - Number of readings taken in each period.

k - Constant in Newton's law of cooling for the apparatus.

v_1 - Rate of change of temperature in initial period.

v_2 - Rate of change of temperature in final period.

According to Newton's law.

$$v_1 = k(\theta_o - \theta_1) \qquad v_2 = k(\theta_o - \theta_2)$$

Hence $$k = \frac{v_1 - v_2}{\theta_2 - \theta_1}$$ by eliminating θ_o

In order to obtain the corrected temperature rise we must add to the observed temperature difference, the products of Newton's constant and the area difference $(A_2 - A_1)$ shown in the diagram. The area $(A_2 + A_3)$ equals the sum of the products of successive

temperature differences $(\theta^1 - \theta_1)$ and the unit of time between each observation. For simplicity one minute intervals were used.

$$(A_2 + A_3) = \Sigma (\theta^1 - \theta_1).1$$

Further $(A_1 + A_3) = (\theta_o - \theta_1)(t_2 - t_1) = (\theta_o - \theta_1)Z$

since $(\theta_o - \theta_1) = v_{1/k}$

$$(A_2 - A_1)k = k \Sigma(\theta^1 - \theta_1) - v_1 Z$$

The correction factor obtained $(A_2 - A_1).k$ was added to the observed temperature difference.

Example of heat of reaction measurement.

The heat of solution of fluorosulphuric acid (1.1393g.) in 297.6g. glacial acetic acid. The heat was measured in the Dewar type calorimeter (250 ml. capacity).

Time (mins.)	Resistance (ohms)	Time (mins.)	Resistance (ohms)	Time (mins.)	Resistance (ohms)
0	→1679.20	14	1628.75	28	1577.0
1	1678.78	15	→1628.58	29	1567
2	1678.35	16	1588.7	30	1556.5
3	1677.91	17	1589.7	31	1551.8
4	→1677.50	18	1590.55	32	1551.65
5	1670.6	19	1591.20	33	→1551.88
6	1659.5	20	1591.75	34	1552.23
7	1647.5	21	1592.17	35	1552.55
8	1637.5	22	→1592.62	36	1552.88
9	1630.2	23	1592.88	37	1553.25
10	1629.55	24	1593.13	38	→1553.60
11	→1629.25	25	1593.38		
12	1629.09	26	→1593.63		
13	1628.91	27	1587.0		

→ The beginning and end of each heating or cooling period.

Time 1 to 4 First constant Newtonian period. After 4 mins. the calibration heater was turned on for 4 mins. and constant Newtonian condition reached after 11 mins. until 15 mins. when the chemical reaction was started by breaking the ampoule of fluorosulphuric acid. Newtonian conditions again held at 22 mins. until 26 when the second 4 min. calibration run was carried out. From 33 to 38 mins. the final Newtonian period was recorded. During the electrical calibration runs current and voltage readings were recorded every minute.

The thermostat temperature was 24° and the experimental temperature range was 23.5 to 25.5°. The Newtonian periods appear to be short but experience with the calorimeter showed that constant rates were quickly reached and maintained and longer periods did not improve accuracy. With the metal calorimeter (b) larger and slightly variable rates were obtained, hence longer Newtonian periods were measured to keep possible errors to a minimum.

Time (mins.)	Voltage (volts)	Current (amps)	Time (mins.)	Voltage (volts)	Current (amps)
4-5	0.28926	0.29190	26-7	0.28925	0.29184
5-6	0.28927	0.29190	27-8	0.28925	0.29184
6-7	0.28927	0.29188	28-9	0.28922	0.29180
7-8	0.28925	0.29184	29-30	0.28926	0.29179
Mean	0.28926	0.29187		0.28924	0.29182
Heating Time	240.13 secs.			240.85 secs.	

The drop in current readings is due to the resistance of the heater slightly increasing with rise in temperature (difference of 1 in 6,000). Although this is not significant it shows that

it is more accurate to measure both current and voltage rather than one of these and assume the resistance is constant. Before calculations were performed all resistance values were converted to temperature in the computer programme. (See p.44)

Programme for computer.

The corrected temperature rises (ΔT corr.) were obtained using the method previously described. The calibration heat rises were then equated to the known heat imputs.

$$\text{Electrical Heat Imput} = \frac{1}{4.1840} \times T \times C \times V \times \frac{(R_3 + R_4)}{R_4} \text{ cal.}$$

T - Time of heating period in seconds.

C - Current. V - Voltage. R_3 - Variable resistance (usually set at 5,620 ohms) R_4 - fixed resistance (215.25 ohms).

The heat of chemical reaction is then obtained by comparison with the electrical calibration experiments.

$$\text{Heat of reaction} = \left(\frac{\text{Heat Imput}}{\Delta T_{\text{corr.}}}\right)_{\text{calibration}} \left(\frac{\text{I+II}}{2}\right) \times (\Delta T_{\text{corr.}})_{\text{reaction}}$$

The heat of reaction per mole was obtained by multiplying the measured heat of reaction by the molecular weight and dividing by the weight of reactant. The computer printed out values for the heat imput divided by the corrected temperature rise for both calibration runs and also the heat of chemical reaction per weight of substance used in calories.

For the heat of solution of fluorosulphuric acid in glacial acetic acid. Cal = calibration

$$\left(\text{Heat Imput} / \Delta T_{\text{corr.}}\right)_{\text{Cal I}} = 68.09$$

$$\left(\text{Heat Imput} / \Delta T_{\text{corr.}}\right)_{\text{Cal II}} = 68.09$$

Hence:-

Heat of reaction I = 107.1)
II = 107.1) Mean 107.1 calories.

This value was then corrected for the value of the substandard 1 ohm resistor used in the circuit and the heat of breaking of the ampoule. The values of the resistances used were checked from time to time.

Calibration of 1 ohm resistor.

The substandard resistor (±0.2%) was checked against a standard 1 ohm resistance by direct substitution in the circuit. The value was checked each month and did not vary significantly. (1 in 10,000 over 1 year)

$$\text{Heat/mole} = \frac{(107.1 - 0.3) \times 1.000 \times 100.07}{1.1393}$$

$$= 9.58 \text{ kcal./mole}$$

Thus the heat of solution of fluorosulphuric acid in acetic acid = 9.58 kcal./mole.

Conversion of resistance readings to temperature.

The error in not converting resistance readings to temperature is described by Wadsö[6]. The relationship $\Delta T \propto (\log R_{1/R_2})$ was initially used but this was found to be in error. The relationship $T \sim {}^{1}/_{\log R_1}$ or $\Delta T = T_2 - T_1 \sim {}^{(\log R_1 - \log R_2)}/_{(\log R_1 . \log R_2)}$ or $\sim \log \frac{R_1}{R_2}$

The product $\log R_1 . \log R_2$ is nearly constant over a small temperature but in the calorimetric technique used there was approximately 1-2° difference between the mean temperatures of the two calibration runs. The error in assuming $\log R_1 . \log R_2$ constant is approximately 1%/60 ohm resistance or 1° temperature change. Hence all readings were converted to temperature.

The thermistors used were calibrated against a Beckmann thermometer (See p 29)

For the thermistor used in the Dewar type vessels

$$A = 0.05341 \text{ and } B = 3,070$$

For the thermistor used in the metal calorimeter

$$A = 0.04368 \text{ and } B = 3,087$$

Subsidiary heat corrections.

1) Heat of breaking of ampoules in Dewar type calorimeter.

a) Glass ampoules for introduction of liquids = 0.30 ± 0.06 cal.

b) Glass cover slips for introduction of solids = 0.45 ± 0.10 cal.

2) Heat of breaking of ampoules in nickel plated brass calorimeter.

a) Aluminium foil. Two thicknesses of Al. foil were used to seal each end. Three plunges at 60° intervals were used to break the foil. The errors in determining the heat of breaking have been described previously. Heat of breaking = 0.20 ± 0.05 cal.

b) Teflon foil. This was used for mild reactions in BrF_3. The foil was pretreated with hot BrF_3 before use. The foils were ruptured by thrusting three times (at 60° intervals) onto the knife fitted to the base of the can. The heat of breaking of Teflon foil was much higher than with metal foils due to the strength of the foil and the attack on the foil after the ampoule was broken. Despite the fact that the surface area of Teflon, exposed to attack from BrF_3, was doubled on breaking reasonably consistent results were obtained for the heat of breaking.

Heat of breaking = 1.40 ± 0.10 cal.

3) The heat of transference of Br_2/BrF_3 in the "twin-cell" calorimeter.

The reactants were mixed by suction on the Br_2/BrF_3 mixture in one cell to the solid reactant in the other cell. The heat

of transference was measured in the absence of reactant. The main heat effect was due to a small vaporization of the volatile constituents. Heat of transference = -1.20 ± 0.20 cal.

Calibration of calorimeters by Standard Reactions.

The Dewar type calorimeter and the nickel plated brass calorimeter were tested with two of the recommended standard reactions[7]. This checked not only the performance of the calorimeter used but also the computer programme and the techniques used.

Comparison of standard reactions were carried out by Gunn[7] who suggested the following desirable characteristics for a comparison process.

(1) The process should consist of mixing a weighed amount of a standard substance, solid or liquid, in a fragile bulb or other sample chamber with a large volume of a liquid which should be water or an aqueous solution.

(2) The process should be rapid and complete.

(3) An exothermic process would be more desirable than an endothermic one.

(4) The heat of reaction per mole should be reasonably large so a reasonable temperature rise is obtained without using a large amount of reactant.

(5) The heat should be well defined at 25°, and the temperature coefficient should be small around this temperature.

(6) The heat of dilution should tail off so that small changes in the ratio of standard substance to liquid and to the concentration of solutes, if any, in the initial liquid are unimportant.

(7) Exposure of the liquid to the atmosphere should have a negligible effect on the heat.

(8) The heat should be the same whether the calorimeter is open or closed or the difference should be readily calculated.

(9) No gases should be evolved.

(10) The change of vapour pressure of the liquid should be small.

(11) The change in volume of the liquid should be small.

(12) The volume occupied by the sample chamber should be no more than 5% of the liquid volume, and preferably less.

(13) The mass of the standard substance used should be large enough for convenient and accurate weighing.

(14) The heat capacity of the substance should be small.

(15) The standard substance should be available in high purity or should be easily purified.

(16) The standard substance should be non-hygroscopic, non-volatile and non reactive with the atmosphere.

(17) The standard substance should not be subject to significant energy perturbations from crystal defects, internal strains or surface energy effects.

The heat of solution of KCl in water and the heat of neutralization of tris(hydroxymethyl)aminomethane (hereinafter designated T.H.A.M.) with 0.1N hydrochloric acid were used to check the process used.

The heat of solution of potassium chloride in water was suggested by Mischenko and Kaganovich[9] as a standard process for calibration of reaction calorimeters. Gunn[10] and, Sunner with Wadso[5], have also examined this system but concluded that the process is not entirely satisfactory. One obvious disadvantage is the endothermicity whereas the majority of reactions studied are exothermic. Gunn[7] examined the effect of some variations in the treatment of the KCl before for use as a

calorimetric standard.

Preparation		$KCl.\ 200H_2O$
(a) 18 hours at 105°	same material	4,195.7 ± 0.9
(b) 16 hours at 720°	same material	4,202.8 ± 0.9
(c) Fused in air and cooled slowly	same material	4,199.9 ± 1.4
(d) Optical quality random sized pieces cleaved into plates about 1 mm. thick		4,203 ± 0.5

Other disadvantages of KCl as a standard are:

1) The temperature coefficient of solution heat at room temperature is too high (36 cal./mole per °centigrade).

2) On a molar basis the heat of solution of KCl is low and hence may be easily influenced by impurities, crystal habit and size and dissolved gases in the water.

3) The heat of solution per mole is rather small.

However as only medium accuracy was required and using the information and data reported by Gunn[7] and Sunner[3] it was decided to test the calorimeters (a) and (b) using the heat of solution of KCl in 275 moles H_2O.

AnalaR grade KCl was finely ground, dried at 110° for 24 hours and stored in a desiccator over $CaCl_2$.

Wadsö and Irving[11] have recently proposed the heat of neutralisation of T.H.A.M. with aqueous hydrochloric as a calorimetric standard. The reaction seems quite suitable for calorimetric comparison especially because T.H.A.M. has properties qualifying it as a primary acidimetric standard. This heat of neutralisation was used as another method of assessing the calorimetric technique.

Purification: T.H.A.M. (99% purity) was purified as described by Fossum, Markunas and Riddick[12].

60g. T.H.A.M. was dissolved in 120 ml. distilled water and

warmed to 60°. Carbon (5g.) was added and the mixture maintained at 50° to 60° for 30 minutes with constant stirring. The mixture was filtered hot and the treatment repeated. The filtrate was nearly colourless. The solution was concentrated to 130 ml. and T.H.A.M. precipitated by adding the solution to 400 ml. methanol with continuous stirring. The solution was allowed to cool for 30 mins. then cooled to 3°. The mother liquor was filtered off and the solid washed with methanol and the slurry rapidly filtered. For the second recrystallisation the amine was added to 100 ml. H_2O and concentrated to 100 ml. then poured into 300 ml. methanol. For the third recrystallisation T.H.A.M. was added to 80 ml. distilled water, concentrated to 80 ml. then added to 250 ml. methanol. The mixture was cooled, filtered and washed with methanol. The solid was air dried between filter papers, finely ground and finally dried in a vacuum desiccator over P_2O_5 for 7 days at 0.5 mm. Hg over that period. The vacuum was released just prior to use.
M.P. of T.H.A.M. = 117.0°. The purity of the recrystallised T.H.A.M. was obtained by titrating against 0.1NHCl using 0.1% Alizarin RedS and Bromocresol green as indicator. The purity of T.H.A.M. used for a calorimetric standard was 99.8 to 99.9% pure.

Standard Reactions.

1) Heat of solution KCl in 275 moles H_2O.

Dewar type calorimeter:-

Wt KCl (g)	Wt H_2O (g.)	H_2O/KCl (M)	Heat evolved /mole KCl cal. corrected to 25° (13)(14)
3.7354	248.3	275	-4,190
3.7379	249.2	275	-4,203
3.7362	248.2	275	-4,214
		Mean	-4,202 ± 8

Nickel Plated Brass calorimeter:-

Wt KCl (g.)	Wt H_2O (g.)	H_2O/KCl (M)	Heat evolved /mole KCl cal. corrected to 25° (13)(14)
2.2526	151.0	276	-4,190
2.2537	150.1	276	-4,200
2.2511	150.6	276	-4,220
		Mean	-4,203 ± 12

Both the values obtained compare favourably with the most probable value - 4,204 ± 3

2) Heat of neutralisation of T.H.A.M. with O.1NHCl.

Dewar type calorimeter:-

Wt T.H.A.M. (g.)	Wt O.1NHCl (g.)	Heat evolved/mole (cal.)
1.4340	250.0	7,130
1.4703	250.0	7,120
1.6971	250.0	7,090
2.4268	250.7	7,100
	Mean	7,110 ± 15

Nickel Plated Brass calorimeter:-

Wt T.H.A.M. (g.)	Wt 0.1NHCl (g.)	Heat evolved/mole (cal.)
1.2920	172.8	7,080
1.0900	172.8	7,090
0.9473	173.1	7,120
0.8013	168.8	7,130

Mean 7,105 ± 20

Once again the values obtained compare favourably with the most probable heat of neutralisation = 7,111 ± 2 cal.

The above results show that the apparatus and the technique were satisfactory. The small error in the heats of neutralisation of T.H.A.M. may be due to the different concentrations of reactant used.

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CHAPTER II

THE HEATS OF FORMATION OF FLUORO- AND CHLORO-SULPHURIC ACIDS AND THEIR THERMODYNAMIC STABILITIES

The heat of formation of chlorosulphuric acid was determined by Ogier[1] both by hydrolysing the acid and by combining sulphur trioxide with hydrogen chloride. There is insufficient data in his paper to correct the auxiliary heats to present day values. The heat of formation of fluorosulphuric acid was determined by Woolf[2] who mixed hydrogen fluoride dissolved in fluorosulphuric acid with an excess of sulphur trioxide in the same solvent. The derived heat of formation involved an estimate of the heat of solution of hydrogen fluoride in fluorosulphuric acid and neglected the heat of polymerisation of hydrogen fluoride. More recently the overall heat of reaction of gaseous sulphur trioxide with hydrogen fluoride and condensation to a solution of sulphur trioxide in fluorosulphuric acid has been measured on a semi technical scale[3]. The derived heat of formation of fluorosulphuric acid is optimistically given an accuracy of $\pm$2%. Again the heat of polymerisation of hydrogen fluoride is neglected. Since the heat of formation of chloro- and fluoro-sulphuric acids are required to measure the heats of formation of chloro- and fluorosulphates they were determined more precisely. To obtain the heats of formation of chlorosulphates the value for chlorosulphuric acid is not required since they readily hydrolyse to chloride and sulphate. However chlorosulphuric acid could be used in displacements reactions as with fluorosulphuric acid. The extent of possible dissociations of the acids can be assessed by combining the heats of formation with free energy functions[4] and comparing them with experimental observations.

The heat of formation of fluorosulphuric acid determined by mixing sulphur trioxide with excess hydrogen fluoride in fluoro-

sulphuric acid was 190.7±0.6 kcal./mole at 25°. The heat of formation of chlorosulphuric acid determined by hydrolysing the acid was 143.5±0.4 kcal./mole. The reaction of hydrogen chloride with excess sulphur trioxide in fluorosulphuric acid yielded a confirmatory value of 144.2±0.6 kcal./mole. The value for the heat of formation of hydrogen fluoride, required in deriving that of fluorosulphuric acid, was obtained by measuring the heat of hydrolysis of iodine pentafluoride. The heat of formation of the latter has been determined directly from the elements.

Experimental.

All heats of reaction were measured in the nickel-plated brass calorimeter (b).

Results.

1) The heat of formation of fluorosulphuric acid

This was obtained from the heat of reaction of sulphur trioxide with excess hydrogen fluoride dissolved in fluorosulphuric acid.

a) The heat of solution of hydrogen fluoride in fluorosulphuric acid. Fluorosulphuric acid was prepared by bubbling hydrogen fluoride into cooled sulphur trioxide in a stainless steel beaker. It was purified by distillation in "Pyrex" glass distillation apparatus, the fraction boiling at 163° being collected.

It has been reported by Gillespie[5], and it will be later proved thermochemically, that freshly distilled fluorosulphuric acid contains a variable excess of sulphur trioxide. Before determining the heat of solution it is essential to add an excess of hydrogen fluoride to remove any free sulphur trioxide

or the reaction of hydrogen fluoride with excess sulphur trioxide would swamp the heat of solution. Hydrogen fluoride (mid-fraction from a cylinder of grade suitable for fluorine generators) was condensed into a copper container and immersed in the thermostat at 24°. Hydrogen fluoride was introduced by opening a stainless steel needle valve and the gas was passed through a long copper coil in the thermostat then through a nickel tube into fluorosulphuric acid in the calorimeter. The amount of hydrogen fluoride added was found by the change in weight of the copper container and the calorimeter. The changes in weight of the two containers were the same indicating that all the hydrogen fluoride passed, had dissolved and no fluorosulphuric acid had been lost by evaporation. The amount of hydrogen fluoride dissolved does not need to be known accurately (i.e. to better than 10 mg.) because the heat of solution is small and any error in the weight of hydrogen fluoride dissolved has little effect on the final value for the heat of formation of fluoro-sulphuric acid.

TABLE I

The heat of solution of hydrogen fluoride in fluoro-sulphuric acid.

HF (g.)	Initial solution HF (g.)	Initial solution HSO_3F (g.)	Final Solution HF/SO_3 (mole ratio)	ΔH/mole HF dissolved (kcal.)
2.12	6.92	203.8	1.22	1.25
1.87	2.00	199.4	1.10	1.29
3.05	3.87	200.9	1.16	1.42

Mean value 1.32 ± 0.07

b) The heat of reaction of sulphur trioxide with excess hydrogen

fluoride in fluorosulphuric acid. (Table II)

Sulphur trioxide was distilled from oleum (65% W/W free sulphur trioxide), containing potassium persulphate to remove any dissolved sulphur dioxide, into thin walled glass ampoules under a stream of dry nitrogen. Polymerisation of sulphur trioxide was avoided by using freshly distilled samples for calorimetry. The heating effect due to the attack by the solution of hydrogen fluoride in fluorosulphuric acid on the Pyrex glass ampoules containing sulphur trioxide was measured. Attack on the glass ampoules will occur throughout the calorimetric run originally on the outer surface and on both inner and outer surfaces after the ampoule is broken. To determine this heat effect glass ampoules were sealed then placed under 18 g. hydrogen fluoride in 106 g. fluorosulphuric for approximately one hour, then washed with methylene chloride, alcohol and finally dried. A mean weight loss of 1.4 mg./hr. was found (0.5 mg./sq.cm./hr.). The solution used for these experiments contained five times the concentration of hydrogen fluoride as the solutions used for reaction with sulphur trioxide. The main constituents of Pyrex glass are silicon dioxide and boron trioxide and if they are both converted to their fluorides the heat of attack on glass under these extreme conditions will be no greater than 0.06% of the reaction heat and thus can be neglected.

The heat of polymerisation of hydrogen fluoride, the enthalpy difference between the real gas and the monomer, was derived from the data of Franck and Meyer[6] as described later. The values obtained in kcal. per 20 g. of substance at 760 mm Hg. 5.32 (20°), 5.09 (22°), 4.93 (24°), 4.80 (25°), 4.66 (26°), 4.35 (28°), 4.00 (30°), 3.62 (32°) and 3.23 (34°). The value

TABLE II

Wt.SO_3 (g.)	Initial solution Wt.HF (g.)	Wt.HSO_3F (g.)	HF/SO_3 (mole ratio)	ΔH/mole HSO_3F formed (kcal.)
0.8510	8.7	181.3	1.23	13.62
0.7187	8.5	179.5	1.21	13.71
0.6224	8.3	177.6	1.23	13.56

Mean value 13.62 ± 0.09

of 4.86 kcal. was chosen because the heat of solution of hydrogen fluoride was measured at a mean temperature of 24.5°. This heat together with $-\Delta H_f$ $SO_3(l)$ = 105.4[7], $-\Delta H_f$ HF(g) = 65.5 (see discussion) and the heats in Tables I and II yield $-\Delta H_f$ $HSO_3F(l)$ = 190.7 ± 0.6. The heat of formation of the vapour is obtained by adding the heat of vaporization of 10.0 kcal./mole.

The heat of vaporization of fluorosulphuric acid, at 163°, reported was 8.4 kcal./mole[3], and a value of 10.0 kcal./mole estimated for 25°. ΔHvap./$_{\Delta T}$ was obtained by comparison with compounds of similar boiling points.

Compound	Temp.(°C)	Heat of vaporization kcal./mole	ΔHvap./$_{\Delta T}$ kcal./mole/°
CBr_4	190	10.6	$1.6/_{165}$
	25	12.2	
$TiCl_4$	137	8.65	$1.25/_{112}$
	25	9.9	
H_2O_2	158	10.3	$1.9/_{133}$
	25	12.2	
HSO_3F	163	8.4[3]	$1.6/_{138}$
	25	10.0 (estimated)	

APPARATUS USED FOR PURIFICATION

OF CHLOROSULPHURIC ACID

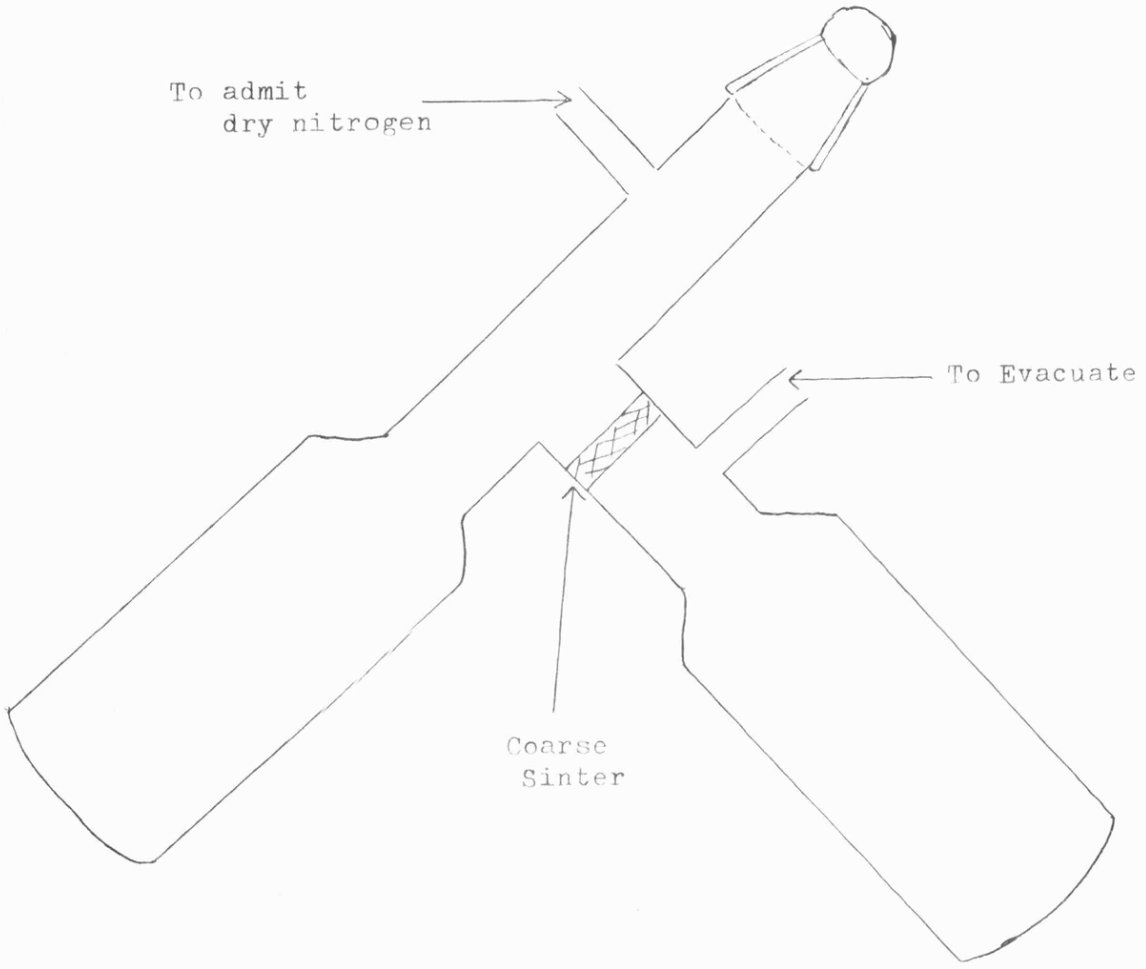

Fig. 7.

Then $-\Delta H_F^\circ\ HSO_3F_{(g)} = 180.7 \pm 1.2$. The main uncertainty in this value is due to heat of formation to be ascribed to polymeric hydrogen fluoride.

2) The heat of formation of chlorosulphuric acid by hydrolysis

The violence of the reaction

$$HSO_3Cl + H_2O = H_2SO_4 + HCl$$

was controlled by placing baffles in the calorimeter to eliminate splashing. Commercial grade chlorosulphuric acid was re-distilled and then purified by fractional freezing in an ethanol-"drikold" bath at atmospheric pressure under a stream of dry nitrogen to eliminate atmospheric moisture. A 200 ml. sample was partially frozen and the mother liquor filtered off through a sinter (No.3 porosity) in the same apparatus (see Fig.7). After five more fractionations the remaining 10 - 15 ml. of acid was syringed into thin-walled glass ampoules. Vacuum filling was avoided because of possible decomposition even at room temperature. After hydrolysis aliquots of the solution were analysed alkalimetrically, with phenolphthalein as indicator, for total acidity and for chloride ion by Mohr's titrations with silver nitrate using potassium chromate as indicator. This confirms the purity of the chlorosulphuric acid used.

TABLE III

Hydrolysis of chlorosulphuric acid

	Wt. HSO_3Cl (g.)	Wt. H_2O (g.)	H_2O/HSO_3Cl (mole ratio)	ΔH/mole (kcal.)
(a)	0.3884	150.0	2,500	41.57
(b)	0.4310	152.1	2,280	41.74
(c)	0.3856	150.0	2,520	41.74

Mean value = 41.68 ± 0.07

HCl GENERATOR

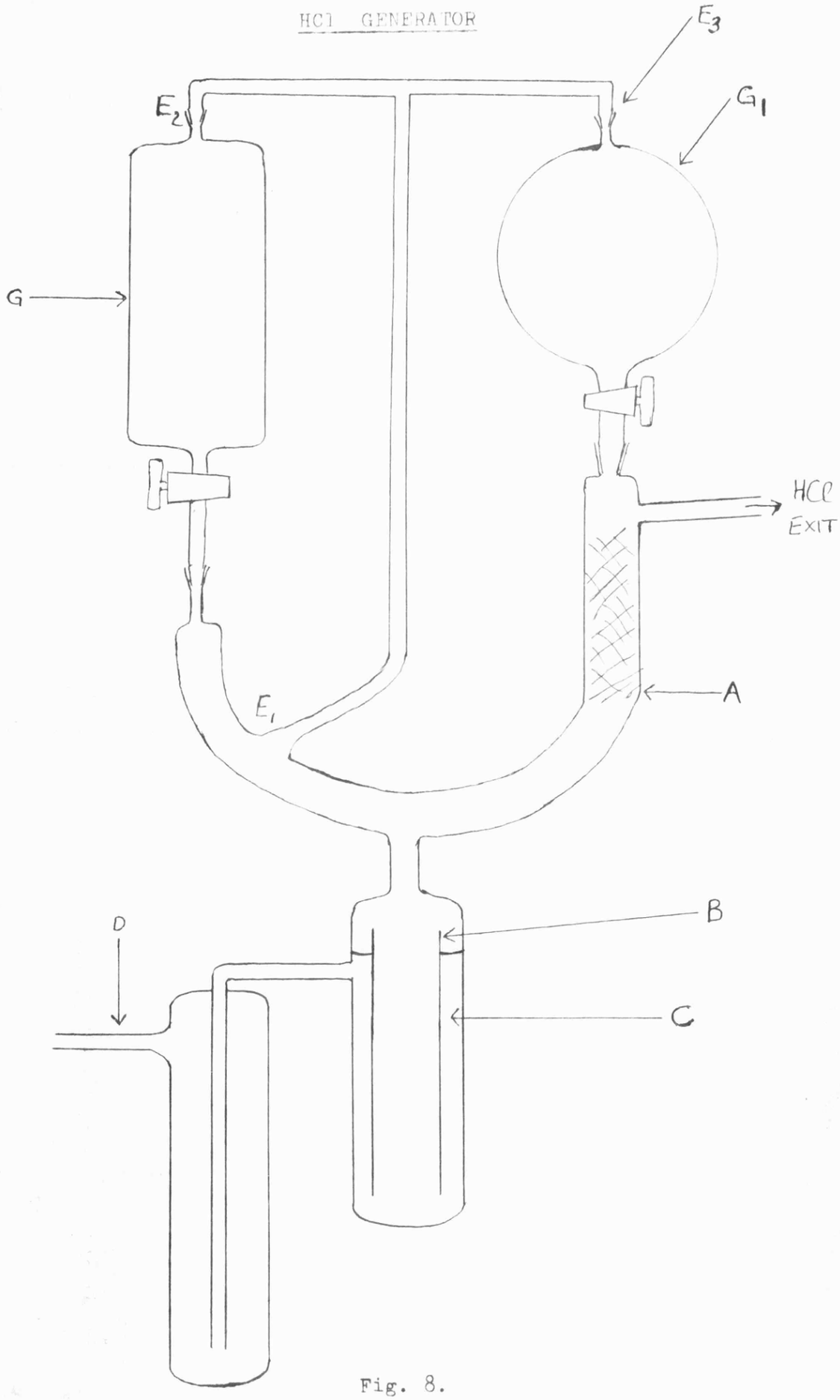

Fig. 8.

TABLE IV

Analysis of Hydrolysis Products

	H^+ (mg.)		Cl^- (mg.)		H^+/Cl^- (g.atoms)
	Found	Calc.	Found	Calc.	
(a)	10.08	10.00	118.2	116.4	3.03
(b)	11.18	11.15	131.2	130.2	3.01
(c)	10.01	9.96	117.3	116.9	3.00

Using the auxiliary heats $-\Delta H_f$ HCl, $2500H_2O$ = 39.95, $-\Delta H_f H_2O$ = 68.32, $-\Delta H_f H_2SO_4$ $2250H_2O$ = 213.5 and $-\Delta H_f$ H_2SO_4 2,500 = 213.6[9][10] $-\Delta H_f$ chlorosulphuric acid (liquid) at 25° = 143.5 ± 0.4 kcal.

3) The heat of formation of chlorosulphuric acid

From the reaction of hydrogen chloride with excess of sulphur trioxide in fluorosulphuric acid.

The heat of formation of chlorosulphuric acid was determined by the above method and not by breaking sulphur trioxide under excess hydrogen chloride because if the latter were used the heat of solution of hydrogen chloride in fluorosulphuric acid would have to be determined. When hydrogen chloride is bubbled into fluorosulphuric acid hydrogen fluoride may be displaced because the reaction is virtually balanced thermochemically, and the standard free energy change is small (-2.6 kcal.).

$HSO_3F + HCl = HSO_3Cl + HF$ (in HSO_3F) -2.6 kcal.

The heats of solution of sulphur trioxide and chlorosulphuric acid in fluorosulphuric acid were determined by breaking ampoules of the former under fluorosulphuric acid. Hydrogen chloride was generated by dropping concentrated sulphuric acid on to concentrated hydrochloric acid using the apparatus described by Harwood and Tucker[38], (see diagram opp.)

The dropping funnels were of 250 ml. capacity, G contained hydrochloric acid and G_1 contains concentrated sulphuric acid which dries the hydrogen chloride generated by countercurrent flow. An indentation at A prevents the glass wool moving. The acids were mixed in annulus B, the unreacted and spent acids passed over into C to complete mixing then out via exit D. All connections were made of P.V.C. tubing between E_1, E_2 and E_3. Kel-F grease was used on the joints. When generating hydrogen chloride the glass wool was flooded with sulphuric acid, then the acids were dripped in together, sulphuric acid being added twice as fast as hydrochloric acid. The issuing gas was further dried by passing through an ethanol - solid carbon dioxide trap and collected in a 250 ml. bulb. The bulb was then immersed in the thermostat at 24°. The reaction of hydrogen chloride with excess sulphur trioxide in fluorosulphuric acid was measured by displacing the hydrogen chloride with dry mercury, the rate of displacement (166 ml./min.) being controlled by the mercury flow through a capillary on the inlet side. The issuing gas was bubbled through a coarse sinter to ensure as complete a reaction as possible. The amount of hydrogen chloride which reacted was determined potentiometrically (see Appendix III) on a hydrolysed aliquot with silver nitrate (0.05N). The hydrolysis of 5 ml. of the final solution was carried out in a closed system slowly adding the solution from a dropping funnel fitted with a Teflon tap to an ice-cooled aqueous solution of 11 g. sodium hydroxide. Any hydrogen chloride in the gas phase was absorbed by aqueous alkali in a wash bottle on the exit side. The hydrolysate (200 - 300 ml.) was neutralised with acetic acid and then acidified with 5 ml. of 8N nitric acid. The silver

nitrate was standardised against synthetic solutions of the same composition. The chlorine content of the sodium hydroxide used was deducted.

TABLE V

The heat of solution of sulphur trioxide in fluorosulphuric acid.

Wt. SO_3 (g.)	Wt. HSO_3F (g.)	HSO_3F/SO_3 (mole ratio)	ΔH/mole SO_3 (kcal.)
0.9227	191.0	166.1	1.63
0.7017	187.4	213.6	1.64
0.8391	189.1	180.1	1.62

Mean value = 1.63 ± 0.01

TABLE VI

The heat of solution of chlorosulphuric acid in fluorosulphuric acid.

Wt. HSO_3Cl (g.)	Wt. HSO_3F (g.)	HSO_3F/HSO_3Cl (mole ratio)	ΔH/mole HSO_3Cl (kcal.)
0.9370	206.5	256.8	-0.28
0.5969	272.8	532.5	-0.21
0.7548	294.0	453.7	-0.21

Mean value = -0.23 ± 0.03

The heat of breaking of the glass ampoules was allowed for in these small heats of solution (ca. 0.3 cal.)

TABLE VII

The heat of reaction of hydrogen chloride with excess of sulphur trioxide in fluorosulphuric acid.

Wt. HCl (g.)*	Wt. HSO_3F (g.)	Wt. SO_3 (g.)	HSO_3F/HSO_3Cl (mole ratio)	ΔH/mole HCl (kcal.)
0.3690	221.7	6.4	220	14.92
0.3571	191.4	5.8	196	14.93
0.3595	208.9	6.2	213	15.11

Mean value = 14.99 ± 0.08

*By analysis.

The heat of formation of HSO_3Cl calculated from the above heats and $-\Delta H_f$ HCl = 22.06 kcal. was - 144.2 $\pm$ 0.6 kcal./mole. The hydrolysis value is more reliable because fewer auxiliary heats were required and the analysis was more precise.

Determination of the excess sulphur trioxide in freshly distilled fluorosulphuric acid.

Excess sulphur trioxide in fluorosulphuric acid has been determined by Gillespie[5] by displacement of freezing point concentration curves from the origin.

Fluorosulphuric acid was purified by distillation in glass apparatus, collecting the fraction boiling at 162.5 - 163°. Freshly distilled fluorosulphuric acid was put in the calorimeter and the heat of reaction of excess anhydrous hydrogen fluoride with that solution was measured. The amount of hydrogen fluoride added was determined both by the weight loss of the hydrogen fluoride container and the weight gain of the calorimeter respectively.

	HF (g.)	HSO_3F (g.)	Heat per amount HF passed cal.
(a)	0.40	184.5	46.0
(b)	1.05	171.2	72.2

(a) and (b) are different samples of distilled acid.

a) Determination of amount of free sulphur trioxide.

Heat of solution of HF in HSO_3F = 1.32 ± 0.07 kcal./mole

Heat of solution of 0.4 g. HF = $\frac{1.3 \times 10^3 \times 0.4}{20.01}$ = 26 cal.

∴ 20 cal. due to heat of reaction of HF with excess SO_3.

Heat reaction of SO_3 with HF = 13.6 kcal./mole

Amount free SO_3 in 184.5 g. HSO_3F = $\frac{20 \times 80.07}{13.600}$ = 0.117 g. SO_3

In 1000 g. HSO_3F = $\frac{0.117 \times 1000}{184.5}$ = 0.63 g. or 0.008M

b) Amount of free SO_3 = 0.0035M

Amount free SO_3 = 0.0035 to 0.008M

Heat of formation of hydrogen fluoride

Due to the uncertainty in the heat of formation of monomeric hydrogen fluoride (see discussion) it was decided to derive a value from the heat of hydrolysis of iodine pentafluoride whose heat of formation has been recently determined (-211.0 ± 0.5 kcal./mole)[11]. The heat of hydrolysis of iodine pentafluoride with potassium hydroxide was measured.

$$IF_5 + 6KOH = KIO_3 + 5KF + 3H_2O$$

Iodine pentafluoride was prepared from the elements and the colourless midfraction distilled into thin-walled glass ampoules under a stream of dry nitrogen. The purity was determined by

analysis of potassium iodate formed with standard sodium thiosulphate via $KIO_3 \rightarrow I_2$

TABLE VIII

Heat of neutralisation of iodine pentafluoride with aqueous potassium hydroxide.

		IF_5 (g.)	Aqueous KOH (g.)	ΔH per mole IF_5 neutralised (kcal.)
0.88N KOH	a)	2.1651	259.5	118.56
	b)	1.6057	261.2	118.33
			Mean	118.45 ± 0.11
	c)	2.5199	255.1	118.73
0.50N KOH	d)	3.1316	255.3	119.04
	e)	3.0635	254.4	118.92
			Mean	118.89 ± 0.10

After hydrolysis the solutions were analysed for KIO_3.

	KIO_3 (g.) found	KIO_3 (g.) calculated from weight IF_5	KF (g.) Theo.	KF + KIO_3 (g.) Theo
a)	2.086	2.088	2.834	4.922
b)	1.547	1.548	2.102	3.650
c)	2.4363	2.4391	3.2973	5.7377
d)	3.0335	3.0328	4.0980	7.1307
e)	2.9640	2.9667	4.0088	6.9757

The heat of solution of the products in aqueous potassium hydroxide was measured. A mixture of 5KF:KIO_3 was prepared, finely ground and the ratio was confirmed by analysis.

TABLE IX

Heat of solution of $5KF/KIO_3$ in aqueous potassium hydroxide.

		$5KF/KIO_3$ (g.)	Aqueous KOH (g.)	Heat evolved per $5KF/KIO_3$ dissolved kcal.
0.88N KOH	a)	4.9221	260.0	13.77
	b)	3.6503	260.0	13.73
			Mean	= 13.76 ± 0.02
0.50N KOH	c)	5.7377	255.1	14.20
	d)	7.1307	254.8	13.96
			Mean	= 14.08 ± 0.12

Total heat of reaction (1) In 0.88NKOH = 104.7 ± 0.11

(2) In 0.5NKOH = 104.8 ± 0.14

$$IF_5 + 6KOH_{aq} = 5KF + KIO_3 + 3H_2O + 104.75 \text{ kcal.}$$

$-\Delta H_f, H_2O$ 68.32; IF_5 211.0; KIO_3 119.7 (see later); $KOH.63H_2O$ = 115.1[12] give $-\Delta H^\circ_f$ KF = 136.3 kcal./mole.

thus $-\Delta H_f HF_{(gas)}$ = 65.7 ± 0.3 kcal./mole (allowing for new value of KOH)

The heat of formation of potassium iodate was redetermined by measuring the heat of reaction of potassium iodate solution with excess potassium iodide (10 g.) in 250 ml. NHCl.

$$KIO_3 + 5KI + 6HCl = 6KCl + 3I_2 + 3H_2O$$

Potassium iodate solution was used because when solid KIO_3 reacts with KI the iodine formed deposited on the KIO_3 crystals retarding complete reaction.

10.025 g. KIO_3 was dissolved in 100 ml. water and a 5 ml. aliquot of this solution used for reaction with potassium iodide. The amount of potassium iodate added per 5 ml. was determined by analysis, 0.5000 g. being added on each occasion. Three heats of reaction were measured and the heat of reaction per mole KIO_3 = 82.24 ± 0.20 kcal. (82.54, 82.10, 82.08).

The heat of solution of the reaction products in N.HCl was measured, this heat included the heat of reaction $I_2 + KI = KI_3$, theoretical quantities ($3I_2/6KCl$) of the products being used.

I_2 (g.)	KCl (g.)	NHCl (g.)	Heat evolved per ($6KCl/3I_2$) dissolved (kcal.)
1.8010	1.0579	252.0	-27.10
1.8010	1.0578	252.0	-27.24
1.8010	1.0584	252.0	-26.96

Mean = -27.10 ± 0.09

Hence the overall heat of reaction = 109.34 ± 0.23 kcal./mole

Combining the heats measured with auxiliary data, $-\Delta H_f$, $KI.230H_2O$, 73.85 (Based on revised HI value reported by Skinner)[14]; $HCl.55H_2O$, 39.60; KCl, 104.18 and H_2O, 68.32 gives $-\Delta H_f\ KIO_3.12H_2O = 113.82$, hence $-\Delta H_f KIO_3 = 119.9 \pm 0.30$ kcal./mole. This is in accord with the value reported by Skinner[13], $-\Delta H_f KIO_3 = 119.5 \pm 0.2$ and calls for revision of the value reported in NBS Circular 500. In all calculations a value of -119.7 kcal./mole was used for the heat of formation of potassium iodate.

The value obtained for the heat of formation of potassium fluoride produces a value of -65.7 ± 0.3 kcal./mole for the heat of formation of hydrogen fluoride. A possible source of error in the value obtained lies in the uncertainty in the value used for the heat of formation of IF_5 because it is contaminated with IF_7 when iodine is burnt in fluorine and thorough analysis of the mixture is required. However the IF_7 estimation in IF_5 seems satisfactory. Firstly only 10% excess F_2 was used and the IF_7 content kept to only 5%. The amount of IF_7 was estimated in three ways,

1) The bomb was evacuated, F_2 pumped off, and the vapour pressure

of the remaining IF_5-IF_7 mixture was measured. The component values differ sufficiently to provide an accurate estimation of compositions.

2) The mixture was dissolved in alkali when $IF_7 \longrightarrow IO_4^-$ which was estimated. Trial runs showed IF_7 yielded 95% IO_4^-.

3) The amount of the two compounds was estimated from infra-red spectra.

The value for the heat of formation of hydrogen fluoride also rests heavily upon the value adopted for potassium hydroxide. The revised value selected is 0.3 kcal. more stable from the value in NBS Circular 500.

A value for the heat of formation of hydrogen fluoride, independent of KOH, could be obtained by hydrolysis of IF_5 with H_2O. This was performed by Woolf[15], mole ratio H_2O/IF_5 = 1200.

$$IF_5 + 3H_2O = HIO_3 + 5HF + 22.05$$

The heats of formation of IF_5 and HIO_3 have been revised recently $-\Delta H_f\ HIO_{3(aq.)} = 53.3$; $IF_5 = 211.0$ then HF = 65.3 ± 0.4 kcal./mole.

DISCUSSION

It is almost inevitable when studying the heats of formation of fluorides from reaction calorimetry, that there is a great dependence on the heat of formation of hydrogen fluoride. This is a most imperfect gas and is a complex mixture at normal temperatures and pressures. There has been considerable uncertainty in the value to be ascribed to the heat of formation of monomeric hydrogen fluoride. Despite several reports on the heat of formation of hydrogen fluoride a reliable "final" value

has not been obtained. To illustrate this point, recent work on the heat of formation of ideal gas hydrogen fluoride is listed below.

Method	Author(s)	-Heat of formation (kcal.)
1. The heat of combustion of ammonia in the constant pressure fluorine flame calorimeter. Correction for non-ideality of the gas is based on data of Strohmeier and Briegleb[16].	Armstrong and Jessup[8]	64.63 ± 0.07
2. The heat of reaction of fluorine with excess hydrogen at 100° to avoid any correction for non-ideality.	von Wartenburg and Schutza[17]	64.45 ± 0.1
3. U.V. dissociation limit of dilute hydrogen fluoride using correction factor of Simons and Hildebrand[23].	Johns and Barrow[22]	65.1 ± 0.4
4. Combined heat of combustion of silica in fluorine with the heat of hydrolysis of silicon tetrafluoride as determined by Lenfesty et. al.[19]	Feder, Wise, Margrave, and Hubbard[18]	64.92 ± 0.12
5. Enthalpies of solution of lithium fluoride, lithium hydrogen fluoride, hydrogen fluoride, the enthalpy of mixing lithium fluoride solution with hydrofluoric acid and the enthalpy of dissociation of lithium hydrogen fluoride .	Cox and Harrop[20]	65.9 ± 0.12
6. Heat of reaction of nitrogen trifluoride with hydrogen to form nitrogen and hydrogen fluoride.	Sinke[39]	65.5 ± 0.2

Method	Author(s)	-Heat of formation (kcal.)
6.(Contd.) There are three independent methods for the heat of formation of NF_3: (a) Sinke[21], from the heat of explosion of NF_3; (b) Walker[40] from heat of reaction of sulphur with $NF_3 \rightarrow SF_6$; (c) Ludwig and Cooper[41] heat of reaction of boron with NF_3 to form BF_3. The heats of formation obtained are (a) -31.44 ± 0.3, (b) -31.75 ± 0.2 and (c) -31.95 ± 1.3 kcal./mole. Accepting the mean of (a) and (b) as the "best" available $\Delta H_f\ NF_{3(g)}$ = -31.6 ± 0.2		
7. Heat of hydrolysis of IF_5 with aqueous KOH, $\Delta H_f\ IF_5$ = -211.0 ± 0.5 kcal./mole by fluorine bomb calorimetry (Jeffes and O'Hare)[11]	This thesis	65.7 ± 0.3
8. Combination of their heat of formation of $BF_{3(g)}$ with measurements by Gunn[43] (heat of reaction of BF_3 with aqueous HF) and by Good and Mansson[44] (of the heat of formation of HBF_4 solution).	Johnson, Feder and Hubbard[42]	65.6 ± 0.1
9. Heat of formation of CF_4 (graphite + F_2) combined with the heats of combustion of the same sample of Teflon in O_2 and F_2	Hubbard[24]	65.5 ± 0.2 or 65.3 ± 0.2

Method	Author(s)	-Heat of formation (kcal.)

9.(Contd.)

$$C_2F_{4(s)} + 2F_{2(g)} \rightarrow 2CF_{4(g)} \quad (25)$$

$$C_2F_{4(s)} + O_{2(g)} + 42H_2O_{(l)} = 2CO_{2(g)} + 4\left[HF.10H_2O\right]_{(l)} \quad (26)$$

The two values obtained are due to the uncertainty in $\Delta H_f CF_4$.

Further values for the heat of formation of hydrogen fluoride would be obtained by accurately measuring the heat of hydrolysis of tungsten hexafluoride and molybdenum hexafluoride.

$$MF_6 + 6NaOH = MO_{3(aq)NaOH} + 6NaF_{(aq)NaOH} + 3H_2O$$

where M = Mo or W.

The heats of formation of molybdenum and tungsten hexafluorides have been accurately determined by Hubbard[27][28] using fluorine bomb calorimetry. The heats of hydrolysis of the two hexafluorides have been measured but the results reported are insufficiently precise for determining the heat of formation of sodium fluoride and then the heat of formation of hydrogen fluoride.

The heat of hydrolysis of rhenium heptafluoride would give an even better value since it gives 7 moles of hydrogen fluoride. The heat of formation of ReF_7 could easily be determined by fluorine bomb calorimetry.

$$2ReF_7 + 16NaOH = 2NaReO_4 + 14NaF + 8H_2O$$

The heat of formation of $NaReO_4$ is known.

The value selected for the heat of formation of hydrogen fluoride was -65.5 kcal./mole which is the value reported by both

Hubbard; Sinke; and Johnson,Feder and Hubbard. The value listed in NBS Technical Bulletin 270-1 is -64.9 kcal./mole which appears to be low compared with the values obtained by Cox, Hubbard, Sinke and myself. However the situation remains unsatisfactory and more confirmatory values for the heat of formation of hydrogen fluoride are required before the matter can be regarded as settled.

In order to calculate the heat of formation of the real associated gas, the data reported by Franck and Meyer[6] was used as it was derived under conditions most akin to ours. They determined heat capacities by measuring the temperature gradient along a nickel capillary tube subjected to an applied potential and through which passed nitrogen or hydrogen fluoride. The former gas was used as a calibrant.

To obtain the enthalpy difference between the ideal and real hydrogen fluoride gas, the graph of heat capacity against temperature at 750, 760 and 770 mm Hg was plotted and from a graphical integration the value was obtained. Franck and Meyer reported specific heats against pressure at various temperatures and a short extrapolation (721 to 760 mm Hg) provides the specific heat at the temperature and pressures used in the calorimetric runs.

The specific heat of hydrogen fluoride gas was measured to 105°, at this temperature it is assumed to be monomeric and the specific heat at this temperature = 7.4 cal./20g.HF. The specific heat of the monomer is virtually temperature independent and no assumption is made about the composition of the polymeric mixture.

TABLE X

Specific heat data reported by Franck and Meyer.

	Pressure (mm.)									
T°C	116	230	319	420	519	623	721	750	760	770
24	14.8	60.0	143.0	218.2	219.6	183.0	143.0	132.6	128.6	124.4
25	13.4	53.8	129.2	206.6	218.2	190.0	156.0	145.0	141.6	138.0
26	12.2	48.4	113.6	195.5	214.0	197.4	168.5	159.6	156.8	154.0
30	11.0	34.0	70.0	145.0	194.0	218.0	200.0	193.2	191.6	189.4
35	9.6	15.6	50.2	82.0	134.0	202.0	212.9	212.0	211.0	207.0
40	8.2	11.0	23.0	44.6	72.0	118.6	185.0	200.8	205.6	209.0
45	8.0	9.2	12.0	23.0	38.6	68.0	124.6	141.0	146.6	152.0
50	7.8	8.4	11.4	17.1	23.0	37.8	67.4	83.0	90.0	100.0
55	7.7	8.0	9.2	12.6	15.0	22.0	36.0	48.4	54.0	61.0
60	7.6	8.0	9.1	9.6	11.0	15.0	22.0	28.4	32.0	36.4
65	7.6	7.6	8.2	8.9	9.4	11.8	16.6	20.0	22.0	26.8
70	7.6	7.5	7.9	8.2	8.0	9.7	12.4	14.6	15.8	16.6
75	7.6	7.5	7.7	7.8	7.7	9.4	10.0	10.8	11.6	12.0
80	7.6	7.4	7.5	7.6	7.5	7.7	7.9	8.0	8.2	8.3
85	7.5	7.3	7.4	7.5	7.4	7.5	7.7	7.7	7.7	7.7
90	7.5	7.2	7.4	7.4	7.4	7.4	7.5	7.5	7.5	7.5
95	7.4	7.1	7.3	7.3	7.3	7.3	7.4	7.4	7.4	7.4
100	7.3	7.1	7.3	7.2	7.3	7.3	7.4	7.4	7.4	7.4

The area under the graph of specific heat against temperature at constant pressure was measured and the enthalpy difference between the monomer and real gas is recorded in Table XI. In Table X values at 750, 760 770 mm Hg were obtained by extrapolation.

TABLE XI

Temperature °C	$(H_T^{ideal} - H_T^{real})$ cal.		
	750 mm Hg	760 mm Hg	770 mm Hg
20	5140	5320	5450
22	4940	5090	5250
24	4780	4930	5090
24.5	4720	4860	5030
25	4650	4800	4960
26	4510	4660	4820
28	4200	4350	4510
30	3850	4000	4160
32	3470	3620	3780
34	3080	3230	3390

Hydrogen fluoride was introduced into the calorimeter at atmospheric pressure and 24.5°.

Wt. HF (g.)	Wt. HSO_3F (g.)	Temp. React. (°C)	Heat soln. (kcal./mole)	Rate of flow mg./sec.
1.87	201.4	24.2 - 25.0	1.29	5.2
3.05	204.8	24.0 - 25.5	1.42	5.65
2.12	210.7	24.0 - 25.0	1.25	5.90

The flow rate of hydrogen fluoride used by Franck and Meyer was 6.5 mg./minute. Allowing for the diameters of the tubing used, the flow rate was 50 mg./mm.^{2}/min. for heat of solution experiments compared with 3 mg./mm.^{2}/min. for specific heat measurements. The value used to compensate for the associated nature of hydrogen fluoride was 4.86 kcal./mole. An error of $\pm$ 0.13 kcal. arises from a temperature uncertainty of $\pm$ 1° in the heat capacity measurements and another 0.1 kcal. from

pressure variations of ± 10 mm Hg caused by change in atmospheric pressure and depth of immersion of the inlet tube in the calorimeter and an unknown error from our faster flow rate. Medvedev[29] implies that an indeterminate error exists because no allowance was made for change in molecular composition along the tube in specific heat measurements. An overall error of ±0.3 kcal. in the heat of formation of fluorosulphuric acid seems a reasonable estimate.

The halogenosulphuric acids[1] are associated but to a much smaller extent than HF. The heats of formation which have been determined refer to a polymeric mixture. The infrared and Raman spectra indicate the presence of dimers in the liquid and vapour at room temperature and their absence from the hot vapour[4][30]. The relative amounts of monomer and dimer have not been assessed. In order to determine the equilibrium dissociations of the acids an estimate of dimer concentration shows that the Gef functions for the dimer are slightly more than half the monomer values when calculated on the monomeric molecular weight. Thus up to 10% of dimer in the mixture would not alter the equilibrium constants to any greater extent than the errors inherent in the calorimetric measurements and the effect of dimer content can be neglected to a first approximation.

The relevant thermodynamic quantities are collected in Table XII.

TABLE XII

Thermodynamic quantities of halogenosulphuric acids and decomposition products.

State of substance at °K		-Standard heat of formation (kcal./mole)	-Entropy of formation (cal./deg./mole)	-Free energy of formation (Gibbs) (kcal./mole)
SO_3 in HSO_3Cl	298	107.1	52.05	91.6
SO_3 in HSO_3F	298			
SO_3 (l)	298	105.4	52.05	89.9
SO_3 (g)	298	95.2	20.15	89.2
SO_3 (g)	435	90.7	54.20	67.1
HSO_3F (l)	298	190.7	71.6	169.3
HSO_3F (g)	298	182.3	49.6	167.5
HSO_3F (g)	436	178.0	84.3	141.3
HSO_3Cl (l)	298	143.6	70.4	122.6
HSO_3Cl (g)	298	134.1	48.4	119.7
HSO_3Cl (g)	432	130.1	84.7	93.6
HF (monomer)	298	65.5	-1.6	66.0
HF*	298	70.4	16.0	65.6
HF* in HSO_3F	298	71.5	16.0	66.8
HF (monomer)	436	64.4	-1.6	65.1
HCl	298	22.06	2.4	22.7
HCl	432	21.1	1.2	21.6
HCl in HSO_3Cl	298	23.3	2.4	23.9
SO_2Cl_2(l)	298	94.0	58.0	76.7
H_2SO_4(l)	298			164.6
SO_2F_2 in HSO_3F	298	-183[31]	37.3	-172

*Associated gas at 760 mm Hg

TABLE XIII

Equlibrium constants for dissociation of halogenosulphuric acids.

Equilibrium	Temp. (°K)	-log K
$HSO_3X_{(l)} \rightleftharpoons HX_{(soln)} + SO_{3(soln)}$		
for X = F	298	8.0 ± 1
X = Cl	298	5.3 ± 1
$HSO_3X_{(g)} \rightleftharpoons HX_{(g)} + SO_{3(g)}$		
for X = F	298	9.3 ± 1
X = Cl	298	5.3 ± 1
X = F	436	4.3 ± 1
X = Cl	432	2.5 ± 1
$2HSO_3Cl \rightleftharpoons H_2SO_{4(soln)} + SO_2Cl_{2(soln)}$	298	2.8 ± 1.7
$2HSO_3F \rightleftharpoons H_2SO_{4(soln)} + SO_2F_{2(soln)}$	298	3.0 ± 1.7

Thus acids in the liquid or gaseous state at room temperature cannot be more than slightly dissociated to sulphur trioxide and hydrogen halide, chlorosulphuric acid being the more dissociated. Fluorosulphuric acid is less stable in the gas phase at its boiling point than at room temperature. At its b.p. 0.007 moles of sulphur trioxide and hydrogen fluoride would be in equilibrium with one mole of the acid. The dissociation into sulphuryl fluoride and sulphuric acid is more favourable thermodynamically but it is less feasible kinetically. However, Ruff's[32] experiment (see later) shows a negligible dissociation to sulphuryl fluoride even at higher temperatures. The calculated dissociation of chlorosulphuric acid to sulphuryl chloride and sulphuric acid is far from negligible and could be the main mode

of decomposition if kinetically allowed.

The calculated equilibria accord with experimental observations. Chlorosulphuric acid cannot be distilled without decomposition to H_2SO_4, SO_2, Cl_2, HCl and $S_2O_5Cl_2$[33] (some of the products result from the instability of SO_2Cl_2 and interactions with SO_3). Infrared bands of chlorosulphuric acid were not detected in the super-heated vapour above 170°[30]. However an equilibrium constant of 0.404 with respect to sulphuryl chloride and sulphuric acid has been reported for a reaction in a sealed tube at 170°[34]. Ryadneva and Lenskii[35] noticed the presence of $S_2O_5Cl_2$ and SO_2Cl_2 below 85° and found that the relative amounts varied considerably under varying conditions. It has also been recorded that some hydrogen chloride and sulphur trioxide was found in the dissociated vapour at 40°[30]. Seaman, Woods and Bank[36] found evidence for free sulphur trioxide in chlorosulphuric acid at room temperature by thermometric titration.

Fluorosulphuric acid after distillation in glass apparatus is enriched in sulphur trioxide. This was deduced from the variations in freezing point of different samples as reported by Gillespie[5]. The variable amount of free sulphur trioxide was estimated between 0.004 and 0.007 molal by the displacement of freezing point-concentration curves from the origin. The amount of free sulphur trioxide was determined by thermometric titration with hydrogen fluoride and 0.004 - 0.008 molal quantities were found. From the equilibrium measurements almost 1% of the vapour could be free hydrogen fluoride which could react with the glass oxides and shift the equilibrium before the vapour recondensed. The variations in composition found would then

depend on the kinetics of the attack by hydrogen fluoride on glass and would be a function of the glass surface and the rate of distillation. Ruff[32] passed fluorosulphuric acid through a platinum tube heated at temperatures up to 900° and condensed the issuing vapour. The acid was recovered unchanged except for traces of sulphur dioxide and hydrogen fluoride which he showed were the result of attack of acid on the sulphur used as a sealant. The experiment has been misinterpreted[30] to mean that fluorosulphuric acid vapour is stable at high temperatures whereas it showed that the products which issue from the hot zone reform the acid quantitatively. This is true for the dissociation to hydrogen fluoride and sulphur trioxide but not for the dissociation.

$$2HSO_3F = H_2SO_4 + SO_2F_2$$

Any of the volatile sulphuryl fluoride, which does not react with sulphuric acid, would have been collected.

Hydrogen fluoride was bubbled into chlorosulphuric acid in an unsuccessful attempt to measure the heat of formation of fluorosulphuric acid.

$$HF + HSO_3Cl = HSO_3F \text{ (in } HSO_3Cl) + HCl \text{ (in } HSO_3Cl)$$

The free energy values in Table X demonstrate that the equilibrium constant is small and hence the full displacement of chlorine is difficult. The reverse reaction has been encountered in displacing chlorides with fluorosulphuric acid[37] when chlorosulphuric acid would form to some extent as hydrogen chloride was displaced. The chlorosulphuric acid would decompose to sulphuryl chloride and hence residual chlorine in solution would be removed only slowly.

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CHAPTER III

REACTION CALORIMETRY IN FLUOROSULPHURIC ACID

Fluorosulphuric acid has many of the criteria for a calorimetric liquid; it is easily prepared, purified and recovered; the chemistry in this medium has been established and it has reasonable physical properties at the standard temperature (25^{o})[1]. The thermodynamic data for fluorosulphuric acid was reported in Chapter II.

Reaction calorimetry in fluorosulphuric acid was used initially to determine the heat of formation of potassium fluorosulphate. This value was then used in the scheme to determine the heat of formation of bromine trifluoride. Work in this solvent was extended to determine heats of formation of other fluorosulphates and heats of protonation of organic bases. The types of reaction that have been studied thermally are the production of fluorosulphates by displacement or solvolytic reactions, or by protonation of organic or inorganic substances; and the production of simple or complex fluorides by neutralisation.

The heats of formation of potassium, sodium, cupric, nitrosonium and nitronium fluorosulphates were measured in HSO_3F, and of nitrosonium hydrogen sulphate and disulphate in alkaline hypochlorite solutions. The regularities in heats of formation between perchlorates, hydrogen sulphates and fluorosulphates of the same cation are correlated by heat cycles. The proximity of values for the latter pairs was found empirically. Heats of protonation of water and organic bases in fluorosulphuric acid are approximately related to ionisation in the solvent. Values for the enthalpies and free energies of other ionic fluorosulphates can be estimated from heat cycles or by comparison with hydrogen sulphates. The stability of some unknown

fluorosulphates are predicted.

Apparatus.

All reactions in fluorosulphuric acid were carried out in the nickel plated brass calorimeter and reactions in water or glacial acetic acid were carried out in the Dewar type calorimeter.

Materials.

Fluorosulphuric acid was prepared by passing anhydrous hydrogen fluoride into excess liquid sulphur trioxide in a stainless steel beaker. The mixture was cooled by an ice/salt mixture. Fluorosulphuric acid was purified by distillation in 'Pyrex' glass apparatus at room temperature and the fraction b.p. 163° collected. For the heat of solution in glacial acetic acid, fluorosulphuric acid was distilled into thin walled glass ampoules under a stream of dry nitrogen. The slight excess of sulphur trioxide in fluorosulphuric acid was removed, when necessary for thermal measurements, by adding a slight excess of hydrogen fluoride. Glacial acetic acid was purified by distillation after prolonged heating under reflux with acetic anhydride. The fraction b.p. 118° was distilled into the Dewar type calorimeter under a stream of dry nitrogen. Potassium and cupric acetates were made anhydrous by heating under reflux with acetic acid-acetic anhydride mixture, the solid was filtered off and dried under vacuum. Anhydrous sulphuric acid was prepared by adding oleum (20% W/W free SO_3) to sulphuric acid (95% W/W) until a white fume persisted when a jet of air was directed across the surface. This method is reported to achieve the 100% composition to within 0.01%. Any slight excess of sulphur trioxide in sulphuric acid will not be significant because of the small heat of solution of sulphur trioxide in fluorosulphuric

acid. Potassium fluorosulphate, for heat measurements in acetic acid, was made by neutralisation in acetic acid[2]. Potassium acetate was dissolved in acetic acid-acetic anhydride mixture and the solution was heated under reflux for 14 hours. Fluorosulphuric acid was added to the ice cooled potassium acetate solution and the white precipitate of potassium fluorosulphate was formed. The solid was filtered off, washed with acetic acid, methylene chloride (dried over molecular sieve) then ether and dried under vacuum. Found: K, 28.0; S, 23.0; Calculated for KSO_3F: K, 28.2; S, 23.2%. Potassium and sodium fluorosulphates for use in water or fluorosulphuric acid solutions were made from the persulphates and bromine trifluoride[33]. Excess bromine trifluoride was removed under vacuum. Aqueous solutions were free from sulphate and bromide ions. Cupric fluorosulphate was obtained by the displacement of the acetate in fluorosulphuric acid.

Nitrosonium fluorosulphate was prepared by the action of bromine trifluoride on nitrosonium disulphate[3]. Excess bromine trifluoride was removed and nitrosonium fluorosulphate was heated for 1 hour at 80° under vacuum. Qualitative tests showed the absence of bromide and sulphate ions. Nitronium fluorosulphate was prepared by the action of bromine trifluoride on a mixture of sulphur trioxide and excess dinitrogen tetroxide[3]. Excess dinitrogen tetroxide was used to prevent the formation of the sulphur trioxide-bromine trifluoride compound which has been made by Woolf[3]. Dinitrogen tetroxide was prepared by bubbling sulphur dioxide into 50 ml. fuming nitric acid (95-98%), cooled in an ice-salt mixture, until saturated and a solid mass of nitrosonium hydrogen sulphate was

formed. Powdered potassium nitrate was added and dinitrogen tetroxide distilled into phosphorus pentoxide and redistilled before use.

$$KNO_3 + NO(SO_3OH) = K(SO_3OH) + N_2O_4$$

Nitrosonium hydrogen sulphate was prepared as above. The precipitate was filtered, washed with dry acetic acid then carbon tetrachloride and vacuum dried. Found: S, 25.0; N, 11.0%; Calculated for $NO(SO_3OH)$: S, 25.2; N, 11.0%. Nitrosonium disulphate was prepared by contacting dinitrogen tetroxide and sulphur dioxide in a sealed tube at room temperature for 4 days. Found: S, 27.2; Calculated for $(NO)_2S_2O_7$: S, 27.2%.

Potassium fluoride was prepared by heating the bifluoride at 500°C. Potassium bifluoride was prepared by adding potassium carbonate to excess hydrofluoric acid in a platinum dish. The solution was boiled to remove any carbon dioxide and to concentrate it. Potassium bifluoride was precipitated by ethanol, the solid was filtered, washed with ethanol and dried under vacuum at 40°. An aqueous solution of the purified potassium fluoride was found to be free of hydrogen fluoride and carbon dioxide.

All hygroscopic materials used were stored in a vacuum desiccator over phosphorus pentoxide. The nickel ampoule was filled with reactant and assembled under practically anhydrous conditions. The "dry-box" was fitted with a glass top and elbow length rubber gloves attached to the front. The box was kept dry using alumina and phosphorus pentoxide as desiccants.

Heat of formation.

Throughout these equations, the subscript HA refer to solution in acetic acid, and FS to the solution in fluorosulphuric

acid. Special features of the experiments are noted. Auxiliary heats not quoted were taken from National Bureau of Standards Circular 500 or from the Technical Bulletin 270-1.

The heat of formation of potassium fluorosulphate.

This was determined by measuring the following heats of reaction.

a) $K_2SO_4 + 2HSO_3F = 2KSO_3F + H_2SO_4$

b) $KF + HSO_3F = HF + KSO_3F$

These reactions were carried out in fluorosulphuric acid.

c) Reaction of potassium acetate with an excess and deficiency of fluorosulphuric acid in acetic acid

$$CH_3COOK + HSO_3F = KSO_3F + CH_3COOH$$

TABLE I

Heat of solution of sulphuric acid in fluorosulphuric acid.

H_2SO_4 (g.)	HSO_3F (g.)	HSO_3F/H_2SO_4 (mole ratio)	ΔH per mole of H_2SO_4 dissolved (kcal.)
0.7990	283.5	348	0.24
1.7360	261.1	147	0.21
0.6704	287.4	421	0.24

Mean 0.23 ± 0.01

TABLE II

Heat of solution of potassium fluorosulphate in fluorosulphuric acid.

KSO_3F (g.)	HSO_3F (g.)	HSO_3F/KSO_3F (mole ratio)	ΔH per mole of KSO_3F dissolved (kcal.)
0.8642	294.7	470	8.40
0.6487	297.9	633	8.20
0.5282	296.0	775	8.30

Mean 8.30 ± 0.07

TABLE III

Heats of solution in acetic acid

HSO_3F (g.)	CH_3CO_2H (g.)	CH_3CO_2H/HSO_3F (mole ratio)	ΔH per mole of HSO_3F dissolved (kcal.)
1.5653	239.0	2,545	9.58
1.9168	337.5	2,934	9.54
1.1393	297.6	4,355	9.58
		Mean	9.57 ± 0.02

CH_3CO_2K (g.)	CH_3CO_2H (g.)	CH_3CO_2H/CH_3CO_2K (mole ratio)	ΔH per mole of CH_3CO_2K dissolved (kcal.)
2.5786	248.7	1,577	7.20
2.6746	272.0	1,652	7.06
2.8650	290.4	1,658	7.23
		Mean	7.17 ± 0.07

TABLE IV

Heat of reaction of potassium fluoride and potassium sulphate with fluorosulphuric acid (excess)

	Reactant (g.)	HSO_3F (g.)	HSO_3F/reactant (mole ratio)	ΔH per mole of reactant (kcal.)
	0.8750	277.1	184	26.12
KF	0.6583	273.0	240	25.86
	0.4004	243.8	354	25.90
			Mean	25.96 ± 0.11
	0.8626	269.6	545	41.70
K_2SO_4	0.5160	241.0	816	42.26
	0.3710	279.1	1310	41.85
			Mean	41.93 ± 0.21

TABLE V

Heats of reaction of potassium acetate with excess or deficiency of fluorosulphuric acid in acetic acid.

CH_3CO_2K (g.)	CH_3CO_2H (g.)	HSO_3F (g.)	$CH_3CO_2H/HSO_3F/CH_3CO_2K$ (mole ratio)	ΔH per mole neutralised (kcal.)
2.1407	238.6	4.9	1823/2.2/1	19.10
1.7188	305.6	6.3	2907/3.6/1	18.83
			Mean	18.97 ± 0.13
4.6	227.6	1.4286	2654/1/3.3	22.15
4.2	303.6	1.3048	3878/1/4.9	22.06
			Mean	22.10 ± 0.05

The thermal effect of precipitated potassium fluorosulphate on the reaction was measured by introducing similar quantities of the fluorosulphate into acetic acid. The heat measured was due to a small heat of solution (0.7 g. KSO_3F dissolved in 1000 g. of acetic acid), a heat of ampoule breaking, and a frictional heat due to the presence of precipitate in the liquid.

KSO_3F (g.)	CH_3CO_2H (g.)	CH_3CO_2H/KSO_3F (mole ratio)	Heat evolved (cal.)	cal./g. KSO_3F
2.0337	281.8	3,180	6.8	3.4
1.1985	255.0	4,890	4.6	3.8
1.1460	251.0	5,040	4.2	3.7

The correction amounted to approximately 1.5% of the reaction heat.

$$CH_3.CO_2K + HSO_3F_{HA} = KSO_3F_{HA} + CH_3CO_2H + 19.1 \text{ kcal.}$$

$$HSO_3F + CH_3.CO_2K_{HA} = KSO_3F_{HA} + CH_3CO_2H + 22.1 \text{ kcal.}$$

$-\Delta H_f$ CH_3CO_2K, 173.2; CH_3CO_2H, 116.4; HSO_3F, 190.7; and auxiliary heats yield $-\Delta H_f$ KSO_3F = 276.3 ± 0.2 and

276.8 ± 0.2 kcal./mole respectively.

(a) $KF + HSO_3F = KSO_3F_{FS} + HF_{FS} + 26.0$ kcal.

(b) $K_2SO_4 + 2\ HSO_3F = 2\ KSO_3F_{FS} + H_2SO_{4FS} + 41.9$ kcal.

$-\Delta H_f$ KF, 136.1[4]; HF, 65.5[5]; K_2SO_4, 343.3 and H_2SO_4, 194.6[6][7]; yields $-\Delta H_f$ KSO_3F, 277.7 ± 0.3 and 277.6 ± 0.3 kcal./mole.

Auxiliary heats of solution.

The heats of solution of sulphur trioxide and hydrogen fluoride in fluorosulphuric acid were 1.63 ± 0.01 and 1.32 ± 0.07 kcal./mole respectively as reported in Chapter II.

Heats of formation of other fluorosulphates.

The heats of formation of nitrosonium, nitronium, sodium and cupric fluorosulphates were determined by measuring the following heats of reaction in fluorosulphuric acid

1) $Na_2SO_4 + 2HSO_3F = 2NaSO_3F + H_2SO_4$

2) $NOHSO_4 + HSO_3F = NOSO_3F + H_2SO_4$

3) $(NO)_2S_2O_7 + 2HSO_3F = 2NOSO_3F + H_2S_2O_7$

4) $KNO_3 + HSO_3F = KSO_3F + HNO_3$

then $HNO_3 + 2HSO_3F = NO_2SO_3F + H_3O^+SO_3F^-$

overall $KNO_3 + 3HSO_3F = KSO_3F + H_3O^+SO_3F^- + NO_2SO_3F$

5) $H_2O + HSO_3F = H_3O^+SO_3F^-$

6) $Cu(CH_3CO_2)_2 + 2HSO_3F = Cu(SO_3F)_2 + 2CH_3CO_2H$

The unknown heats of formation of nitrosonium ~~and~~ hydrogen sulphate and disulphate were determined by reaction with alkaline hypochlorite solution.

TABLE VI

Heat of solution of acetic acid in fluorosulphuric acid.

CH_3CO_2H (g.)	HSO_3F (g.)	HSO_3F/CH_3CO_2H (mole ratio)	ΔH per mole of CH_3CO_2H dissolved (kcal.)
0.5430	229.7	254	13.29
0.4989	240.7	290	13.10
0.4501	230.8	307	13.39
		Mean	13.26 ± 0.10

TABLE VII

Heat of solution of water in fluorosulphuric acid.

H_2O (g.)	HSO_3F (g.)	KSO_3F (g.)	$HSO_3F/H_2O/KSO_3F$ (mole ratio)	ΔH per mole of H_2O dissolved (kcal.)
0.4300	218.3	0	91.3/1/0	11.95
0.1937	258.9	0	240/1/0	12.06
0.1606	276.0	0	309/1/0	11.95
			Mean	11.98 ± 0.04
0.1356	231.0	0.455	307/1/0.50	12.30
0.1175	233.5	0.455	358/1/0.68	12.20
0.0711	230.2	0.369	583/1/0.44	11.94
			Mean	12.14 ± 0.14

TABLE VIII

Heat of solution of fluorosulphates in fluorosulphuric acid.

	Fluorosulphate (g.)	HSO_3F (g.)	HSO_3F/MSO_3F (mole ratio)	ΔH per mole of salt dissolved (kcal.)
Na^+	0.6770	297.6	677	7.50
	0.4874	300.1	751	7.43
			Mean	7.47 ± 0.07
NO^+	0.5132	256.0	643	7.44
	0.4441	257.0	747	7.18
	0.3113	258.9	1065	7.43
			Mean	7.35 ± 0.11
NO_2^+	0.7635	264.0	502	6.81
	0.5658	277.4	604	6.90
	0.4780	264.9	805	7.04
			Mean	6.91 ± 0.08

TABLE IX

Heat of reaction of potassium nitrate with fluorosulphuric acid.

KNO_3 (g.)	HSO_3F (g.)	HSO_3F/KNO_3 (mole ratio)	ΔH per mole KNO_3 reacted (kcal.)
0.9525	276.8	294	36.50
0.3048	274.0	908	37.10
0.2915	272.9	975	36.94
		Mean	36.85 ± 0.24

TABLE X

Heat of reaction of sodium sulphate, nitrosonium hydrogen sulphate and disulphate with fluorosulphuric acid.

	Reactant (g.)	HSO_3F (g.)	HSO_3F/reactant (mole ratio)	ΔH per mole reactant (kcal.)
	0.4842	292.3	856	36.35
Na_2SO_4	0.4040	290.7	1021	36.44
	0.3870	295.4	1080	36.27
			Mean	36.35 ± 0.06
	0.9323	281.4	383	10.58
$NO(HSO_4)$	0.8503	290.6	434	10.24
	0.8091	299.4	470	9.70
			Mean	10.17 ± 0.32
	0.6857	274.2	942	28.40
$(NO)_2S_2O_7$	0.6665	266.2	942	31.60
	0.5299	275.3	1225	29.10
			Mean	29.7 ± 1.0

TABLE XI

Heat of reaction of cupric acetate with fluorosulphuric acid.

$Cu(CH_3CO_2)_2$ (g.)	HSO_3F (g.)	$HSO_3F/Cu(CH_3CO_2)_2$ (mole ratio)	ΔH per mole of acetate reacted (kcal.)
0.4200	280.6	1225	40.7
0.5872	264.1	825	41.7
		Mean	41.2 ± 0.5

Cupric acetate was finely ground and a faster stirring rate than usual was used to ensure completeness of this heterogeneous reaction, cupric fluorosulphate having only slight solubility in fluorosulphuric acid. Free sulphur trioxide in the fluorosulphuric

acid was removed initially with hydrogen fluoride. Solution and frictional heats were compensated by saturating the fluorosulphuric acid with cupric fluorosulphate before reactions.

TABLE XII

Heats of reaction of nitrosonium hydrogen sulphate and disulphate with aqueous alkaline solutions of sodium hypochlorite ($^{M}/_{4}$)

	Reactant (g.)	Solution (g.)	H_2O/reactant (mole ratio)	ΔH per mole of reactant (kcal.)
	0.6169	250.0	2860	70.5
$NO(HSO_4)$	0.3813	250.0	4630	69.0
	0.3719	250.0	4740	68.8
			Mean	69.4 ± 0.7
	0.1813	250.0	18,080	159.6
$(NO)_2S_2O_7$	0.4319	250.0	7,580	160.8
			Mean	160.2 ± 0.6

The low precision of these results compared with the alkali fluorosulphates stems from the difficulty in manipulating these hygroscopic salts without decomposition.

$$NOHSO_4 + NaOCl_{aq} + 3NaOH_{aq} = NaNO_{3aq} + Na_2SO_{4aq} + NaCl_{aq} + 2H_2O$$

$$(NO)_2S_2O_7 + 2NaOCl_{aq} + 6NaOH_{aq} = 2NaNO_{3aq} + 2Na_2SO_{4aq} + 2NaCl_{aq} + 3H_2O$$

give $-\Delta H_f$ $NOHSO_4$, 183.2 ± 0.7; $-\Delta H_f$ $(NO)_2S_2O_7$, 276.8 ± 0.6 kcal./mole

Heats of formation of fluorosulphates.

a) Sodium fluorosulphate

$$Na_2SO_4 + 2HSO_3F = H_2SO_{4\,FS} + 2NaSO_3F_{FS} + 36.35 \text{ kcal.}$$

$-\Delta H_f$ Na_2SO_4, 331.6; H_2SO_4, 194.6[6][7]; gives $-\Delta H_f$ $NaSO_3F$, 269.6 ± 0.2 kcal./mole.

b) Nitrosonium fluorosulphate

1) $NOHSO_4 + HSO_3F = NOSO_3F_{FS} + H_2SO_{4FS} + 10.2$ kcal.

2) $(NO)_2S_2O_7 + 2HSO_3F = 2NOSO_3F_{FS} + H_2S_2O_{7FS} + 29.7$ kcal.

The heat of solution of oleum in fluorosulphuric acid was assumed equal to the sum of the heats of solution of sulphuric acid and sulphur trioxide. From the other heats given $-\Delta H_f\ NOSO_3F = 181.3 \pm 0.4$ kcal./mole from (1) and 181.7 ± 1.1 kcal./mole from (2). The former value is chosen as the more reliable.

In an attempt to obtain another value for the heat of formation of nitrosonium fluorosulphate, potassium nitrite was reacted with fluorosulphuric acid, to bring about the reaction,

$$KNO_2 + 3HSO_3F = KSO_3F + NOSO_3F + 'H_3OSO_3F'$$

However inconsistent results were obtained due to nitric oxide and nitrogen dioxide escaping before forming nitrosonium fluorosulphate

i.e. $KNO_2 + HSO_3F = KSO_3F + HNO_2$

$$2HNO_2 + 2HSO_3F = 2"H_3OSO_3F" + NO\uparrow + NO_2\uparrow$$

c) Nitronium fluorosulphate

$KNO_3 + 3HSO_3F = KSO_3F_{FS} + NO_2SO_3F_{FS} + 'H_3OSO_3F_{FS}' + 36.85$ kcal.

The heat of formation of the equilibrium mixture $'H_3OSO_3F'$ in solution was taken as the heat of solution of water in fluorosulphuric acid containing the same amount of fluorosulphate ion as in the above reactions. This quantity is close to the mean of the heats of solution given previously (12.1 kcal.).

Then $-\Delta H_f\ NO_2SO_3F = 162.9 \pm 0.5$ kcal./mole.

d) Cupric fluorosulphate

$Cu(CH_3CO_2)_2 + 2HSO_3F = Cu(SO_3F)_2 + 2CH_3CO_2H_{FS} + 41.2$ kcal.

$-\Delta H_f\ Cu(CH_3CO_2)_2 = 213.2$, $CH_3CO_2H = 116.4$ kcal./mole

and auxiliary heats yield $-\Delta H_f\ Cu(SO_3F)_2 = 376.4 \pm 0.5$ kcal./mole.

TABLE XIII

Heat of solution of sodium fluorosulphate in water.

$NaSO_3F$ (g.)	H_2O (g.)	$H_2O/NaSO_3F$ (mole ratio)	ΔH per mole of salt dissolved (kcal.)
0.7299	250.0	2,320	- 2.81
0.4348	250.0	3,900	- 2.82
		Mean	-2.81 ± 0.01

TABLE XIV

Heats of solution of organic compounds in fluorosulphuric acid.

	Solute (g.)	HSO_3F (g.)	HSO_3F/solute (mole ratio)	ΔH per mole solute dissolved (kcal.)
Benzoic acid	0.7734	284.4	449	8.84
	0.6593	290.0	537	8.60
	0.8726	290.0	405	8.57
	0.7428	291.0	470	9.12
			Mean	8.79 ± 0.19
nitro-benzene	0.3730	192.7	635	5.84
	0.3675	256.5	858	5.48
	0.4767	236.3	609	5.32
			Mean	5.55 ± 0.20
1-Chloro-3-nitro-benzene	0.8734	280.4	504	3.12
	0.9094	277.2	479	3.42
	0.6554	275.6	661	3.58
			Mean	3.37± 0.17
1-Chloro-4-nitro-benzene	1.2084	263.3	342	2.21
	1.5452	318.9	324	1.71
	1.4987	291.5	305	1.43
			Mean	1.78 ± 0.29
2,4 Dinitro toluene	1.2862	272.0	354	0.70
	1.3789	271.4	331	0.30
			Mean	0.50 ± 0.20
1-Chloro-2,4-dinitro benzene	1.6788	304.0	369	-1.56
	1.4250	302.2	431	-1.34
			Mean	-1.45 ± 0.11
nitromethane	0.5722	256.6	274	4.45

Discussion.

The heat of formation of potassium fluorosulphate was determined more thoroughly than other fluorosulphates because it was required as a primary value in two of the reactions, (1) and (2), used to obtain the heat of formation of bromine trifluoride.

$$6K_2SO_4 + 4BrF_3 = 6KF + 6KSO_3F + 2Br_2 + 3O_2 \quad (1)$$

$$3K_2S_2O_8 + 2BrF_3 = 6KSO_3F + 3O_2 + Br_2 \quad (2)$$

It has been established that alkali fluorosulphates can be isolated from displacement reactions on removal of solvent[14]. In solution, the presence of the fluorosulphate ion has been verified directly by the appearance of fluorosulphate ion frequencies (I.R.) at the same values as those of the isoelectronic perchloryl fluoride, when sodium sulphate and sodium chloride are dissolved in fluorosulphuric acid[15]. On warming the solution of sodium chloride in fluorosulphuric acid the hydrogen chloride frequency disappears. Recently potassium fluorosulphate has been prepared by Woolf[2] by a neutralisation reaction in acetic acid[3].

$$CH_3.CO_2K + HSO_3F = KSO_3F + CH_3.CO_2H \quad (3)$$

Potassium fluorosulphate is precipitated from solution. The heat of reaction (3) was measured, with both an excess of potassium acetate and fluorosulphuric acid and an independent value for the heat of formation of potassium fluorosulphate was derived. This value was used to check that the displacement reactions (4) and (5) in fluorosulphuric acid had occurred

$$KF + HSO_3F = HF + KSO_3F \quad (4)$$

$$K_2SO_4 + 2HSO_3F = 2KSO_3F + H_2SO_4 \quad (5)$$

The conductivity of solutions of potassium sulphate in fluorosulphuric acid was measured by Gillespie[1] who confirmed

reaction (5).

The heat of reaction of potassium sulphate and fluoride with fluorosulphuric acid yielded values for the heat of formation of potassium fluorosulphate, concordant between themselves, assuming displacement had occurred, and with the values obtained from neutralisation reaction in acetic acid. The heats of formation obtained from displacement reactions in fluorosulphuric acid were taken as more accurate, experimentally because they were derived in homogeneous solution and theoretically because slight solvolysis of salts in acetic acid[8] would lead to incomplete reaction, the latter effect having greater influence on the accuracy of the value obtained in acetic acid.

Because there are only a few heats of formation of nitrosonium and nitronium salts available, the heats of formation of their fluorosulphates were determined by measuring heats of displacement reactions in fluorosulphuric acid. The expected reactions for the heat of formation of nitrosonium fluorosulphate are (6) and (7),

$$NOHSO_4 + HSO_3F = NOSO_3F + H_2SO_4 \qquad (6)$$

$$(NO)_2S_2O_7 + 2HSO_3F = 2NOSO_3F + H_2S_2O_7 \qquad (7)$$

The heats of formation of nitrosonium hydrogen sulphate and disulphate were redetermined because of the unreliability of the previously reported values[9]. The heats of formation were obtained by decomposing the sulphates in aqueous alkaline solutions of sodium hypochlorite (8) and (9).

$$NOHSO_4 + NaOCl + 3NaOH = Na_2SO_4 + NaNO_3 + NaCl + 2H_2O \qquad (8)$$

$$(NO)_2S_2O_7 + 2NaOCl + 6NaOH = 2Na_2SO_4 + 2NaNO_3 + 2NaCl + 3H_2O \qquad (9)$$

The oxidative hydrolysis avoids errors caused by the instability of the nitrites and the lower accuracy for the heat

of formation of the nitrites compared with the nitrates. Also the heat of formation of sodium hypochlorite solutions has been redetermined recently[32]. Despite difficulty in manipulating the extremely hygroscopic nitrosonium salts reasonably concordant values were obtained for the heats of formation of nitrosonium fluorosulphates confirming the postulated reactions (6) and (7) and the derived heats of formation of the fluorosulphates.

The heat of formation of nitronium fluorosulphate was obtained by measuring the heats of reaction (10) and (11)

$$KNO_3 + 3HSO_3F = KSO_3F + NO_2SO_3F + 'H_3OSO_3F' \quad (10)$$

$$H_2O + HSO_3F = 'H_3OSO_3F' \quad (11)$$

When water is added to fluorosulphuric acid partial hydrolysis and protonation occurs and the following equilibrium is set up (12)

$$'H_3OSO_3F' \rightleftharpoons HF + H_2SO_4 \quad (12)$$

hydroxonium fluorosulphate being in equilibrium with hydrogen fluoride and sulphuric acid. The equilibration (12) is rapid and an accurate value was obtained for the heat of solution of water in fluorosulphuric acid. The composition of the mixture is irrelevant in determining the heat of formation of the nitronium salt provided the second reaction (11) is performed in a medium of the same ionic strength of fluorosulphate as the first (10). The validity of equation (10) has been demonstrated by cryoscopic measurements which indicated the formation of six particles[10]. The number of particles is not dependent upon the position of the equilibrium in (12). Raman spectra of a solution of potassium nitrate in fluorosulphuric acid, gave a sharp line attributed to the nitronium ion, in addition to the other well known lines of sulphuric acid and fluorosulphate ion.

Potassium nitrite cannot be used for the corresponding

thermal measurement, to obtain the heat of formation of nitrosonium fluorosulphate, because of the displacement of nitrogen oxides before nitrosonium fluorosulphate is completely formed.

The heat of formation of the aqueous fluorosulphate ion can be obtained from the heat of neutralisation together with the heat of solution of sodium fluorosulphate (13)

$$HSO_3F_{aq} + NaOH_{aq} = NaSO_3F_{aq} + H_2O \qquad (13)$$

The aqueous acid was formed by passing potassium fluorosulphate through a cation exchange resins[11]. The combination of this value with the heat of formation of aqueous cations yield values for the heat of formation of other ionic fluorosulphates in solution.

The heat of neutralisation of aqueous fluorosulphuric acid is 14.4(6) ± 0.1 kcal./mole[11] and the heat of solution of sodium fluorosulphate in water = -2.81 ± 0.01 kcal./mole. The heat of formation of the aqueous fluorosulphate ion is -207.9 kcal./mole.

The above heats of formation of fluorosulphates are compared with those of the corresponding hydrogen sulphates and perchlorates in Table XV.

TABLE XV

Comparison of heats of formation of fluorosulphates with corresponding salts at 298°K

Fluorosulphates		Hydrogen sulphates		Perchlorates	
NO_2SO_3F	-162.9	$NO_2(SO_3OH)$[a]	-	NO_2ClO_4	8.7
$NOSO_3F$	-181.5	$NO(SO_3OH)$	-182.5	$NOClO_4$	- 9.0[c]
KSO_3F	-277.5	$K(SO_3OH)$	-276.8	$KClO_4$	-103.2
$NaSO_3F$	-269.6	$Na(SO_3OH)$	-269.1	$NaClO_4$	- 91.5
HSO_3F_{aq}	-207.9[b]	H_2SO_{4aq}	-213.4[b]	$HClO_{4aq}$	- 30.9
HSO_3F	-190.7	H_2SO_4	-194.5	$HClO_4$	- 9.7

[a] Dissociates to $(NO_2)HS_2O_7 + HNO_3$. [b] At dilution of 1400 moles of water. [c] See text. (Old value -36.9 kcal./mole).

The values are consistent in that horizontal or vertical differences between pairs of compounds agree within a few kcal. The value reported for nitrosonium perchlorate[12] was not compatible with the above values. The experimental results were recalculated, taking into account the minor changes in heats of formation since the experiment was performed, and the new value is reported in Table XV. The heats of aquation (1500 moles of water) of the three anhydrous acids are 17.2, 18.9 and 21.2 kcal./mole respectively.

The main notable correlation which emerges is the close proximity of values for fluorosulphates and the corresponding hydrogen sulphates. The proximity of the acid values is less close (ca. 5 kcal.) and could reflect differences in stabilisation arising from hydrogen bonding. Sulphuric acid, being hydrogen bonded in three dimensions, might be more stabilised than fluorosulphuric acid which is only bonded in two dimensions. From spectroscopic evidence of hydrogen bonding, are obtained

heat values of 6-11 kcal.[13] and hence differences of the order of 4 kcal. between the heats of formation of fluorosulphuric and sulphuric acid would be just feasible.

It was found empirically that the heats of formation of ionic compounds were not altered appreciably when F is replaced by OH. This comparison can be extended if the hydroxy and fluoro compounds considered are structurally similar. Whatever the detailed explanation a useful corollary is that heats of formation of the other alkali fluorosulphates can be predicted from those of the corresponding hydrogen sulphates.

The interionic forces in fluorosulphates and hydrogen sulphates are expected to be close due to the similarity in the size and charge of the anions. If these are based on the isoelectronic principle then examples of similar heats of formation of isoelectronic anions should exist for a wider range of chemical types. This would serve as a method to check existing data and could be used to predict unknown or inaccessible values. The heats of formation of sulphur and selenium oxyfluorides have been determined in this laboratory and these values are compared with the corresponding hydroxy acids in the liquid state, in Table XVI. The values quoted are corrected for the revised heat of formation of hydrogen fluoride reported in Chapter II.

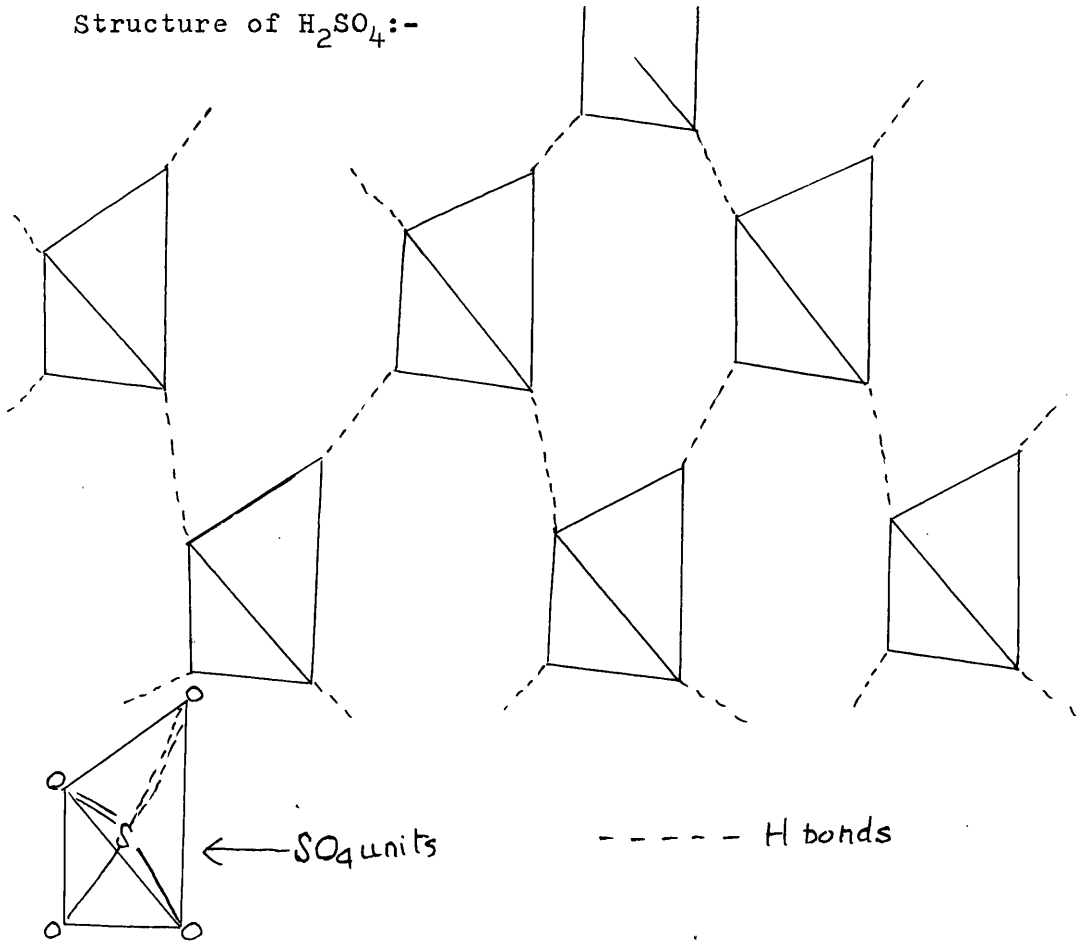
TABLE XVI

-ve Heats of formation of an isoelectronic series of liquids in which F is replaced by OH.

OPF_3	300	O_2SF_2 [16]	187	O_3ClF	10
$OP(OH)F_2$	-	$O_2S(OH)F$ [17]	190	O_3ClOH	10
$OP(OH)_2F$	-	$O_2S(OH)_2$	194		
$OP(OH)_3$	303				

Consider the most reliable series, viz. the sulphur group. There is an increase in stabilisation energy down the series which could be attributed to intermolecular rather than intramolecular forces. Solid sulphuric acid consists of tetrahedral sulphate groups linked by hydrogen-oxygen bonds at each apex in a three dimensional array and on average such a structure is retained in the liquid.

Structure of H_2SO_4:-



The structure of polymeric fluorosulphuric acid is not known but it is polymerised in the liquid state presumably to give a two dimensional array. In fluorosulphuric acid there is a possibility of three types of intermolecular bonding[13],

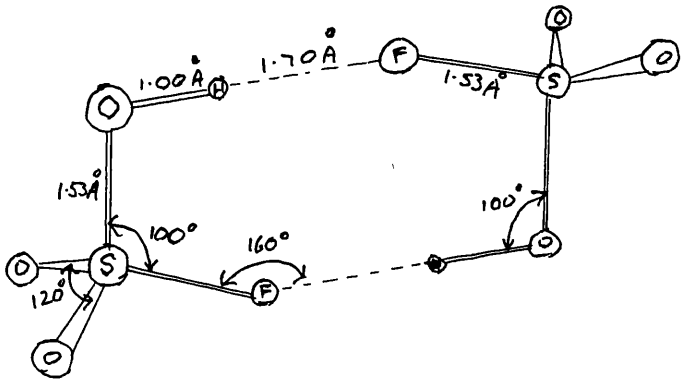
1) With an O - H ..... F bond

2) With an O - H ..... O bond

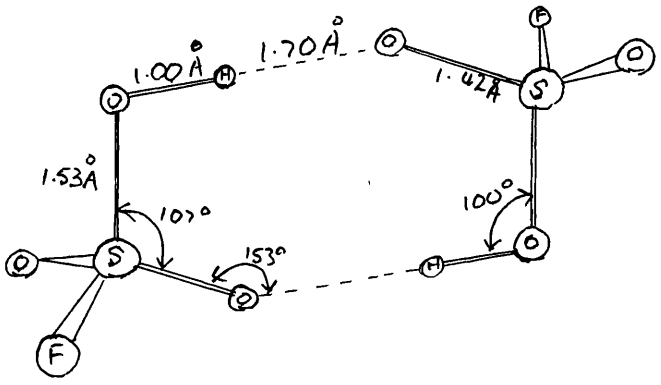
3) A combination of (1) and (2)

Diagram of bonding (1) and (2) in a dimer (assumed parameters)

(i) O - H ..... F bonding.

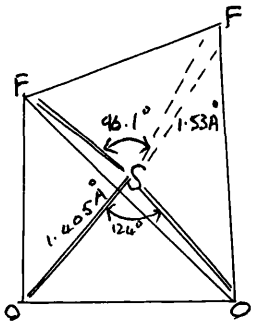


(ii) O - H ..... O bonding.



In a chain polymer each HSO_3F would H-bond to two pairs of different molecules. No hydrogen bonding can occur in SO_2F_2 and the only stabilisation possible is by a much weaker dipole bonding encountered for, e.g. in solid SiF_4. Hence superimposed on the uniform intramolecular forces there is the gradual increasing strength of external forces of the order of magnitude expected for hydrogen bonding.

Structure of SO_2F_2 (tetrahedral)



From the heats of formation of ClO_3F and $HClO_4$ it appears that there is no extra stabilisation in the latter but this may well be obscured by experimental errors. The phosphorus series has not been completed, but it is gratifying that the two end values reported for the series are so close, although a confirmatory value for POF_3 is required.

Partial data is available in the next series, Table XVII.

TABLE XVII

The heats of formation (-ve) of oxyfluorides of arsenic and Selenium and their corresponding hydroxy compounds.

$OAsF_3$	-	O_2SeF_2	118	O_3BrF	-
$OAs(OH)F_2$	-	$O_2Se(OH)F$	125	O_3BrOH	-
$OAs(OH)_2F$	-	$O_2Se(OH)_2$	123		
$OAs(OH)_3$	215				

The heat of formation of fluoroselenic acid had been determined indirectly from a value for an aqueous solution of sodium fluoroselenate formed as one of the hydrolysis products of SeO_2F_2. The heat of formation of $SeO_3F^-_{aq}$ is -141.9 kcal./mole and a heat of hydrolysis of 17 kcal./mole assumed (cf. HSO_3F 17; H_2SO_4 19; H_2SeO_4 17). Assuming the values in Tables XVI and XVII are linearly interconnected the missing values in the latter can be predicted. Thus:

$$\Delta H_f(AsOF_3 - SeO_2F_2) = \Delta H_f(POF_3 - SO_2F_2)$$

gives an estimate for $-\Delta H_f$ $AsOF_3$ of 231 kcal./mole.

Similarly:

$$\Delta H_f(HSO_3F - HClO_4) = \Delta H_f(HSeO_3F - HBrO_4)$$

which gives ΔH_f $HBrO_4$ = + 55 kcal./mole.

The large positive heat of formation and hence large positive free energy is anticipated and $HBrO_4$ has not yet been made.

When considering the fluoro analogues of unstable acids an extension of isoelectronic heats of formation is still possible. These unstable acids have only a slight affinity for water and can be considered thermally as hydrated oxides. In the gas phase sulphurous acid would separate into water and sulphur dioxide and it is possible to equate the heat of formation of thionyl fluoride with the sum of the heats of formation of SO_2 and H_2O.

TABLE XVIII

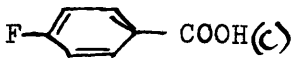
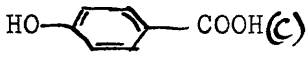
-ve Heats of formation of fluorides compared with the corresponding unstable acids (hydrated oxides).

Fluoride	-Heat of formation	Corresponding Hydrated oxide	-Sum of Heats of formation
$SOF_2(g)$	131	$SO(OH)_2 \rightleftharpoons SO_2(g) + H_2O(g)$	129
$COF_2(g)$	152	$CO(OH)_2 \rightleftharpoons CO_2(g) + H_2O(g)$	152
$TlF_3(s)$	141	$Tl(OH)_3 \rightleftharpoons \frac{1}{2}Tl_2O_3 + 1\frac{1}{2}H_2O(s)$	146
$AuF_3(s)$	88	$Au(OH)_3 \rightleftharpoons \frac{1}{2}Au_2O_3 + 1\frac{1}{2}H_2O(s)$	94

Generally, the structures of fluorides are quite different from hydroxides and the isoelectronic relationship would not hold. When there are close structural resemblances between isolated fluoride molecules with the same shaped hydroxides which are hydrogen bonded, the relationship holds reasonably well. The closer the M-F and M-OH bond lengths, the closer the values for the respective heats of formation.

Compound	-Heat of formation	Bond distance
$BF_3(s)$	276	1.30
$B(OH)_3(s)$	262	1.36
$PF_3(s)$	226	1.535
$P(OH)_3(s)$	232	1.54

The application of the isoelectronic principle for organic compounds should also follow. It is known that F^- and OH^- behave differently, when attached to an organic substrate, as they affect electron distribution. Although there is limited information on heats of formation of analogous fluorides and hydroxy compounds there are some examples for which they are approximately equal.

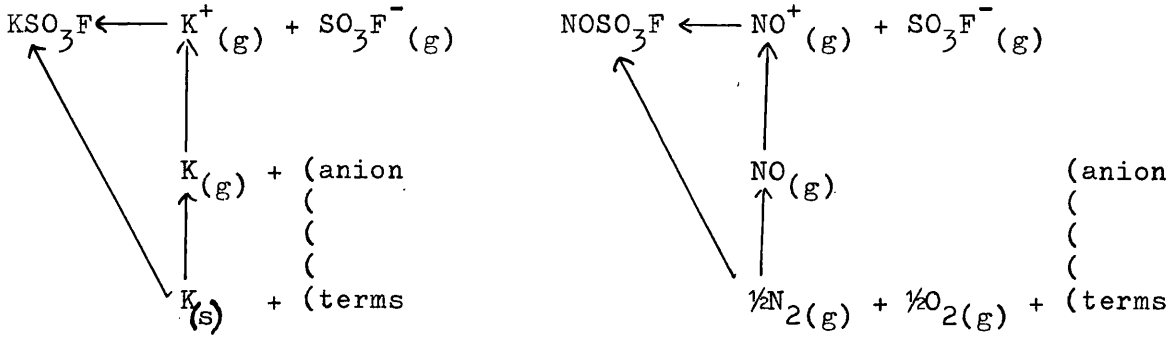
	Compound	-Heat of formation kcal./mole
a)	$C_6H_5F_{(l)}$	36.1
	$C_6H_5OH_{(l)}$	38.9
b)		140.9
		142.8
c)	CH_2FCOOH	162.3
	$CH_2OHCOOH$	158.1

The differences between the heats of formation of the two types of compounds can be rationalised in terms of intermolecular bonding. (a) and (b) the hydroxy compounds have stronger intermolecular bonds hence are more stable. (c) the fluoro acid is a much stronger acid than the hydroxy acid and would form stronger dimers thus becoming more stable.

Finally the simplest example is the comparison of liquid hydrogen fluoride with water, the heats of formation being -72 and -68.3 kcal./mole respectively. The greater stabilisation of hydrogen fluoride can be explained by the stronger H-F bonding than H-O bonding. Association in the vapour is much stronger with hydrogen fluoride than with water vapour.

In principle it is possible to calculate the differences in heats of formation between ionic fluorosulphates via heat cycles of the type shown.

Heat cycles for estimating differences in heats of formation of fluorosulphates.



The difference in the heats of formation between pairs of fluorosulphates is the sum of the differences in heats of formation of the gaseous cations and the difference in lattice energies as all other terms cancel. Data listed in Table XIX enables the heat of formation of the gaseous cations to be estimated.

TABLE XIX

Data for the heats of formation of gaseous cations at 298°K

	Ionisation Potentials[a] (kcal./mole)	Heat of sublimation (kcal./mole)	Heat of formation (kcal./mole)
NO_2	226.5	-	+ 7.9
NO	214.5	-	+21.6
Na	118.5	26.4	0
K	100.1	21.5	0
Cs	89.8	18.8	0
O_2	281.5	-	0
Cl_2	265.2	-	0
ClO_2	256.0	-	24.5
Cu	645.9	80.7	0
Xe	771.6	-	0

(a) First ionisation potential, except for Cu and Xe for which the values reported are the sum of the first and second potentials.

Approximate lattice energies can be obtained from

Kapustinskii's formula[18], although the choice of appropriate cation radius can lead to considerable error. For metal cations the Pauling crystal radii were employed. The effective radius of the fluorosulphate ion, 2.40Å has been measured in metal hexammine fluorosulphates with fluorite lattices[19]. The value selected seems reasonable in view of the close agreement between the crystallographic values obtained for the corresponding isomorphous perchlorates (2.39Å) and the Kapustinskii thermochemical value[18] (2.36Å) which was obtained from heat cycles. The nitrosonium ion appears to have spherical symmetry because the perchlorate is isomorphous with ammonium perchlorate[20]; the NO^+ is spherical due to rotation. If the ion rotates about a point near the mid-position, but slightly nearer the nitrogen nucleus, the radius of 1.06Å (the interatomic distance in NO^+) must be smaller than that of the ammonium ion. A similar estimate of 1.21Å can be made for the dioxygenyl cation.

In the structure of nitronium perchlorate the nitronium cation approximates to cylindrical symmetry[21]. The net positive charge on the nitronium ion is at the centre hence the approximate radius can be taken as equal to that of a sphere of the same volume as the enclosing cylinder. The perchloryl ion is isoelectronic with sulphur dioxide so the radius of the former was taken as that of a sphere which would circumscribe the latter. An approximate xenon cation radius was obtained from the difference between the Xe-F bond length in the difluoride and the radius of the fluoride ion. Although the charge distribution in the difluoride is closer to $Xe^{1.4}(F^{0.7})_2$ the estimated radius of Xe^{2+} would not be altered appreciably. There is reasonable agreement between the calculated and

experimental heats of formation of univalent cations in view of the uncertainties in lattice energy calculations.

The values reported for the ionisation potential of nitrogen dioxide vary from 9.78 to 13.98 ev. Whilst the latter may relate to a higher ionisation potential it is difficult to separate the literature values into groups relating to different electronic levels as they are distributed with some uniformity. The wide range of values is a consequence of change of the size and shape on ionisation, and possibly dissociation of the dioxide. Collin[22] in a recent survey suggested that the lowest values obtained (Mean 9.89), by photoionisation, and indirectly by electron impact values, relates to first ionisation potentials. The first direct measurement by photoionisation shows ionisation down to 9.78 ev. but shows another at 10.83 ev. indentified with the process $NO_2 \longrightarrow NO^+ + O^-$. In the paper by Al-Joboury and Turner[23], it was suggested by Price that the first value might be accounted for by an increase in the photoionisation of nitric oxide following onset of a dissociation process at 9.7-9.8 ev. (evidence for predissociation was obtained from the absorption spectrum). The latter might be accounted for by autoionisation of NO_2. It was concluded by Al-Joboury and Turner that their value (10.97 ev.) was really the only direct measurement of the first ionisation potential of NO_2. The ionisation potential of NO_2 has been redetermined recently by photoionisation[24] and the value reported was 9.75 ev. and this value was used for the calculation of the heat of formation of NO_2^+. This gave a calculated ΔH_f NO_2SO_3F = -178 kcal./mole; using 10.97 ev. a value of -153 kcal./mole is obtained, the measured heat of formation was -163 kcal./mole. The value 10.97 ev. is more

compatible with my results as the calculated differences in the heats of formation of nitronium and nitrosonium salts would be 16 kcal. compared with the experimental differences of 17.7 and 18.6 kcal. for perchlorates and fluorosulphates respectively.

Examples of the predicted values are included in Table XX. Thus Bartlett and Lohmann's[25] justification of the stability of dioxygenyl complex fluorides with very approximate values in a heat cycle are confirmed by the calculated value for the heat of formation of dioxygenyl fluorosulphate. The bivalent xenon fluorosulphate and chloryl fluorosulphate should be stable as ionic salts. An attempt to prepare xenon fluorosulphate by reacting sulphur trioxide with xenon difluoride failed[26]. The overall reaction was (14)

$$2XeF_2 + 4SO_3 = 2Xe + 2S_2O_5F_2 + O_2 \qquad (14)$$

This could represent a decomposition (15) of an intermediate difluorosulphate but since the free energy changes for both reactions are favourable it is not possible to distinguish between them from equilibrium data alone.

$$2Xe(SO_3F)_2 = 2Xe + 2S_2O_5F_2 + O_2 \qquad (15)$$

Evidence for the ionicity of the adduct formed from chloryl fluoride and sulphur trioxide has been reported by Woolf[27].

There is a large difference between the calculated and experimental heats of formation of copper fluorosulphate of approximately 90 kcal. Although calculations are only approximate the difference is significant and is probably due to covalent bonding in $Cu(SO_3F)_2$, which affects lattice energy. If the fluorosulphate group is regarded as a pseudo halogen the above deviation should compare with the differences between the experimental and calculated lattice energies for cupric halides.

The lattice energies of $CuBr_2$, $CuCl_2$ and CuI_2 have been determined from a heat cycle[34] and the values are compared with those calculated using Kapustinskii's equation.

	Compound	(a) Lattice energy from heat cycle (kcal./mole)	(b) Lattice energy from Kapustinskii (kcal./mole)	(a)-(b)
Increasing covalency ↓	$CuCl_2$	670	588	82
	$CuBr_2$	658	562	96
	CuI_2	641	527	114

The partial covalent bonding in $Cu(SO_3F)_2$ is deduced from its solubility in organic solvents and comparison of the S-F stretching frequency with those of other fluorosulphates.

Major contribution in bonding	Fluorosulphate	S-F stretch (cm^{-1})
Ionic	Alkali ions	728-740
	$Cu(NH_3)_6^{2+}$	735
	$Ni(NH_3)_6^{2+}$	730
Covalent	H	850, 837
	CF_3	843
	C_2F_5	
	C_5F_9	849
	F	852
	Cu^{2+}	840

Hence a major contribution to the ionic lattice energy is provided by the covalent contribution which stabilises the lattice.

TABLE XX

Heats of formation of ionic fluorosulphates calculated from heat cycles with respect to potassium fluorosulphate.

Cation	Radius Å	-Heat of formation of fluorosulphate (kcal.) Calculated	Found
Na^+	0.95	267	270
Cs^+	1.69	278	274(a)
NO^+	1.05	169	182
NO_2^+	0.92	(178)(153)(b)	163
O_2^+	1.12	123	-
Cl_2^+	1.89	117	-
ClO_2^+	1.99	99	-
Cu^{++}	0.72	292	384
Xe^{++}	0.64	(259)	-

(a) Value for $CsHSO_4$

(b) Dependent upon ionisation potential of NO_2 (see text).

A value for the heat of formation of hydroxonium fluorosulphate in fluorosulphuric acid was obtained from previous equilibrium data. In fluorosulphuric acid the equilibrium

$$'H_3O^+SO_3F^-' \rightleftharpoons HF + H_2SO_4$$

was obtained from conductivity data assuming that the conductivity of the hydroxonium salt was equal to that of the potassium salt[10]. This is approximately true because of the similarities in the conductivities of the univalent and divalent fluorosulphates which clearly indicated that the major part of the current was carried by the fluorosulphate ion. This conclusion was confirmed by the small values of 0.11 and 0.075 for the cation transport numbers for solutions of potassium and barium fluorosulphate. Thus the fluorosulphate ion carries

approximately 90% of the current. Hydrogen fluoride and sulphuric acid are only very slightly ionised[1]. The heat change (6.8 kcal.) can be calculated from the equilibrium constants of 0.12 and 0.043 at 25° and 0° respectively, using equation (16)

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \qquad (16)$$

Integrating

$$\Delta H = 4.574 T_1 T_2 \frac{(\log K_1 - \log K_2)}{T_1 - T_2}$$

Where ΔH is the mean heat of reaction between temperature T_1 and T_2. K_1 and K_2 are the equilibrium constants at these temperatures respectively.

The heat of formation of hydroxonium fluorosulphate (-257 kcal./mole) follows by adding the heats of formation of hydrogen fluoride and sulphuric acid in fluorosulphuric acid. The feasibility of this value can be assessed by comparing it with that of the isoelectronic ammonium fluorosulphate derived in Table XXI.

TABLE XXI

Derivation of the heat of formation of ammonium fluorosulphate.

	-Heats of formation (kcal./mole)	
	KSO_3F	NH_4SO_3F
Solid	277	244[a]
In HSO_3F	285	253-255[c]
In H_2O	269	239[b]

[a] $-\Delta H_f\ NH_4(SO_3OH)$; [b] $-\Delta H_f\ (SO_3F^-_{aq} + NH_4^+{}_{aq})$;

[c] 244 + 9, 239 + 16, note that 277 + 8 = 285 and 269 + 16 = 285.

There is a close analogy between the hydrolyses of the

fluoroborate (17) and the fluorosulphate (18) ions.

$$BF_4^-(aq) + H_2O = BF_3OH^-(aq) + HF(aq) \quad (17)$$

$$SO_3F^-(aq) + H_2O = SO_3OH^-(aq) + HF(aq) \quad (18)$$

The kinetics of hydrolyses are similar[28] but the equilibrium is much further to the right for the fluorosulphate ion. Ryss[29] obtained a heat of hydrolysis of 3.2 kcal. for the fluoroborate which can be compared with 15.1 kcal. for the fluorosulphate. It should be noted that the free energy and enthalpy changes are almost the same because the entropy changes are only a few entropy units at the most.

If a value for the entropy of the fluorosulphate ion can be assigned then free energy data for fluorosulphates can be estimated. Values between those of the hydrogen sulphate and perchlorate ions are expected. Latimer[30] has reported data for the entropy of the perchlorate ion; 26.0 cal./degree in univalent salts and 22 cal./degree in bivalent salts. Corresponding values 25.7 and 21.2 for hydrogen sulphates can be estimated from the entropies of sulphate, oxide and hydroxide ions $[S(SO_4^{2-}) - S(O^{2-}) + S(OH^-)]$. Similarly the entropy of the aqueous fluorosulphate ion should be between that of perchloric and sulphuric acids in water (43.5 and 37.5 cal./degree respectively). A confirmatory estimate of 40.0 cal./degree was obtained from the empirical equation of Coutoure and Laidler[31] by use of a weighted-mean interatomic distance in the ion of 1.47Å [(3 x S-O distance + S-F distance)/4].

Heats of protonation in fluorosulphuric acid.

The heat of solution of water in fluorosulphuric acid (12.0 kcal./mole) is greater than that derived from the

conductivity measurements (6.8 kcal./mole) because the former includes an additional protonation heat of the water present in the equilibrium mixture. From the equilibrium constant at 25°, 71% of the water is protonated and hence the heat of protonation per mole is 7.2 kcal. This heat of protonation of water can be compared with heats of solution of organic molecules in fluorosulphuric acid in Table XXII.

TABLE XXII

Heats of solution in fluorosulphuric acid in relation to ionisation

Solute	Heat of ionisation (kcal./mole)	State of ionisation ($100K_b$)
HSO_3Cl	-0.23 ± 0.03	Un-ionised[a]
H_2SO_4	0.23 ± 0.01	0.01
HF	1.32 ± 0.07	Slight ionisation as base
SO_3	1.63 ± 0.01	Slight ionisation of HS_2O_6F[b]
1-Chloro-2,4-dinitro-benzene	-1.45 ± 0.11	0.16
2,4-Dinitrotoluene	0.50 ± 0.20	1.4
1-Chloro-4-nitrobenzene	1.78 ± 0.29	76
1-Chloro-3-nitrobenzene	3.37 ± 0.17	7.9
Nitrobenzene	5.55 ± 0.20	Fully ionised
Benzoic Acid	8.80 ± 0.25	Fully ionised
Acetic Acid	13.26 ± 0.10	Fully ionised
Nitromethane	4.46	2.7
KSO_3F	8.30 ± 0.07	Fully ionised
$NaSO_3F$	7.47 ± 0.04	Fully ionised
$NOSO_3F$	7.35 ± 0.11	No figures available[c]
NO_2SO_3F	6.91 ± 0.08	

[a] No direct measurement but since the acid strengths are in the

order $HSO_3F > HSO_3Cl > H_2SO_4$, HSO_3Cl should be less ionized than H_2SO_4 in HSO_3F.

(b) Raman spectral studies have shown that there is a reaction between SO_3 and HSO_3F to form fluorodisulphuric acid. In contrast to $H_2S_2O_7$ in H_2SO_4, HS_2O_6F is not a sufficiently strong acid to ionise to an appreciable extent in fluorosulphuric acid.

(c) From the magnitude of the heat of solution the nitrosonium and nitronium fluorosulphates are most probably fully ionised in fluorosulphuric acid.

The extent of ionisation of organic compounds in fluorosulphuric acid has been measured conductiometrically by Gillespie[1] who determined whether a solute behaves as an acid or a base by adding a small amount of a strong base to a solution of the solute in fluorosulphuric acid and noting the effect on the conductivity of the solution. If the compound is a base then the addition of base merely increases the conductivity of the solution. If the compound is an acid, the addition of base results in a decrease in conductivity due to neutralisation of the acid.

The degree of ionisation of a weak base was found by comparing the concentration of base required to produce a given value of conductivity with the concentration of fully ionised reference base, viz. KSO_3F, required to produce the same conductivity. This method has been used successfully for sulphuric acid solutions; it assumes that the mobilities of the protonated bases are small and that the unionised portion of the weak base has no effect on the conductivity.

If two molecules of similar structure are compared:- one of which is practically unionised and the other fully

ionised; then the difference is likely to be near the heat of protonation, assuming approximately equal heats of solution. Thus in Table XXII, if 1-chloro-2,4-dinitrobenzene is compared with nitrobenzene then the heat of protonation is 7.0 kcal./mole. The absence of any appreciable protonation is also shown by the small heats of solution in agreement with conductivity data. However entropy changes need to be measured before a full correlation can be made. Repression of ionisation by fluorosulphate ion may help to separate the effect of solution heats from the overall heat change.

Proton magnetic resonance spectra of solutions of the organic bases in fluorosulphuric acid proved that no reaction other than protonation had occurred.

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CHAPTER IV

DETERMINATION OF THE HEAT OF FORMATION OF LIQUID BROMINE-BROMINE TRIFLUORIDE MIXTURE AT 25°

The heat of formation of an undersaturated solution of bromine in bromine trifluoride at 25° was obtained by measuring the heats of reaction of this solution with molybdenum and potassium iodate, bromide, sulphate and persulphate. In fluorination reactions with bromine trifluoride, bromine is liberated and the equilibrium mixture obtained.

$$BrF_3 + Br_2 \rightleftharpoons 3BrF$$

It was found that a fairly concentrated solution was most suitable for thermal measurements in view of the heat effect of the above equilibrium. This diminished with increasing bromine content of the mixture. From the following equations, inserting appropriate heats of reaction and solution a consistent value for the heat of formation of the reactive species in solution is obtained, where BrF_3 is written for the actual mixture

$$Mo + 2BrF_3 = MoF_6 + Br_2$$

$$KIO_3 + 2BrF_3 = KF + IF_5 + Br_2 + 1.5O_2$$

$$3KBr + BrF_3 = 3KF + 2Br_2$$

$$3K_2SO_4 + 2BrF_3 = 3KF + 3KSO_3F + Br_2 + 1.5O_2$$

$$3K_2S_2O_8 + 2BrF_3 = 6KSO_3F + Br_2 + 3O_2$$

The heats of formation of potassium persulphate and iodate were redetermined to ensure internal consistency of results. Arguements are advanced for the belief that bromine trifluoride is the reactive species in solution. The value derived for the heat of formation of the bromine-bromine trifluoride solution can be used to determine unknown heats of formation.

The necessity to develop reaction calorimetry with fluoride solvents and the suitability of bromine trifluoride as a calorimetric reaction liquid have been outlined previously (see

Introduction). In this chapter the feasibility of using liquid bromine trifluoride as a general calorimetric reaction medium is established. Bromine trifluoride, or its molten adducts, has the widest potential application of any fluoride since it is capable of reacting with elements or suitable compounds over most of the periodic table[1][2].

Complications could arise in using bromine trifluoride because of the concomitant formation of higher and lower bromine fluorides, BrF_5 and BrF. The equilibria and their thermal effects need to be studied,

$$BrF_3 \rightleftharpoons BrF_5 + BrF$$

$$Br_2 + BrF_3 \rightleftharpoons 3BrF$$

The exact composition of the steady state need not be known accurately provided it is thermally reproducible. Hence the approach has been to show that a reasonably consistent heat of formation can be assigned to equilibrated solutions of bromine fluorides from measurement in a series of reactions of increasing complexity. The value obtained can then be used to determine heats of formation of simple and complex fluorides. Evidence is presented to show that this value derives predominantly from the reactivity of the trifluoride. However the application of reaction calorimetry in bromine-bromine trifluoride solutions does not depend on the validity of this last assumption.

Experimental.

1) Calorimetry

The Dewar type calorimeter was used for aqueous reactions. Mild reactions in bromine trifluoride were carried out in the metal calorimeter (b) and vigorous reactions in the "twin-cell"

calorimeter (c) as described in Chapter I. In the metal calorimeter (b), liquids were introduced in glass ampoules and solids were sealed in the nickel holder with Teflon foil (0.018 cm. thick and pretreated with bromine trifluoride). The heat of attack of bromine trifluoride on the glass ampoules was measured by determining the weight loss of the ampoules (10 mm. diameter) which was 1 mg./hour. The heat evolved from this dissolution was negligible compared with the overall heat measured. In the "twin-cell" calorimeter the small heat of transference of the trifluoride, which amounted to approximately 0.25% of the reaction heats, was allowed for in calculations of molar reaction heats.

2) Materials

Bromine trifluoride was prepared from the elements. Bromine was dried over phosphorus pentoxide before use and fluorine was generated from a 10 amp fluorine cell ex. I.C.I. Description of fluorine cell:-

This was a medium temperature cell operating at 80°-90°. The electrolyte consists of a fused mixture of composition approximately KF. 2HF. The gaseous anhydrous hydrogen fluoride was added to the cell at intervals through a dip-pipe to replace that decomposed by electrolysis.

The cell has a maximum fluorine output of approximately 6.5 g./hour at a pressure not exceeding 5 cm. water.

The cell consists of an electrolyte container surrounded by a controlled heating jacket. The anode is a carbon rod and the wall of the mild steel container serves as the cathode. The fluorine generated may contain some hydrogen fluoride which was removed by passing the gases through a tube containing sodium

BrF_3 DISTILLATION APPARATUS

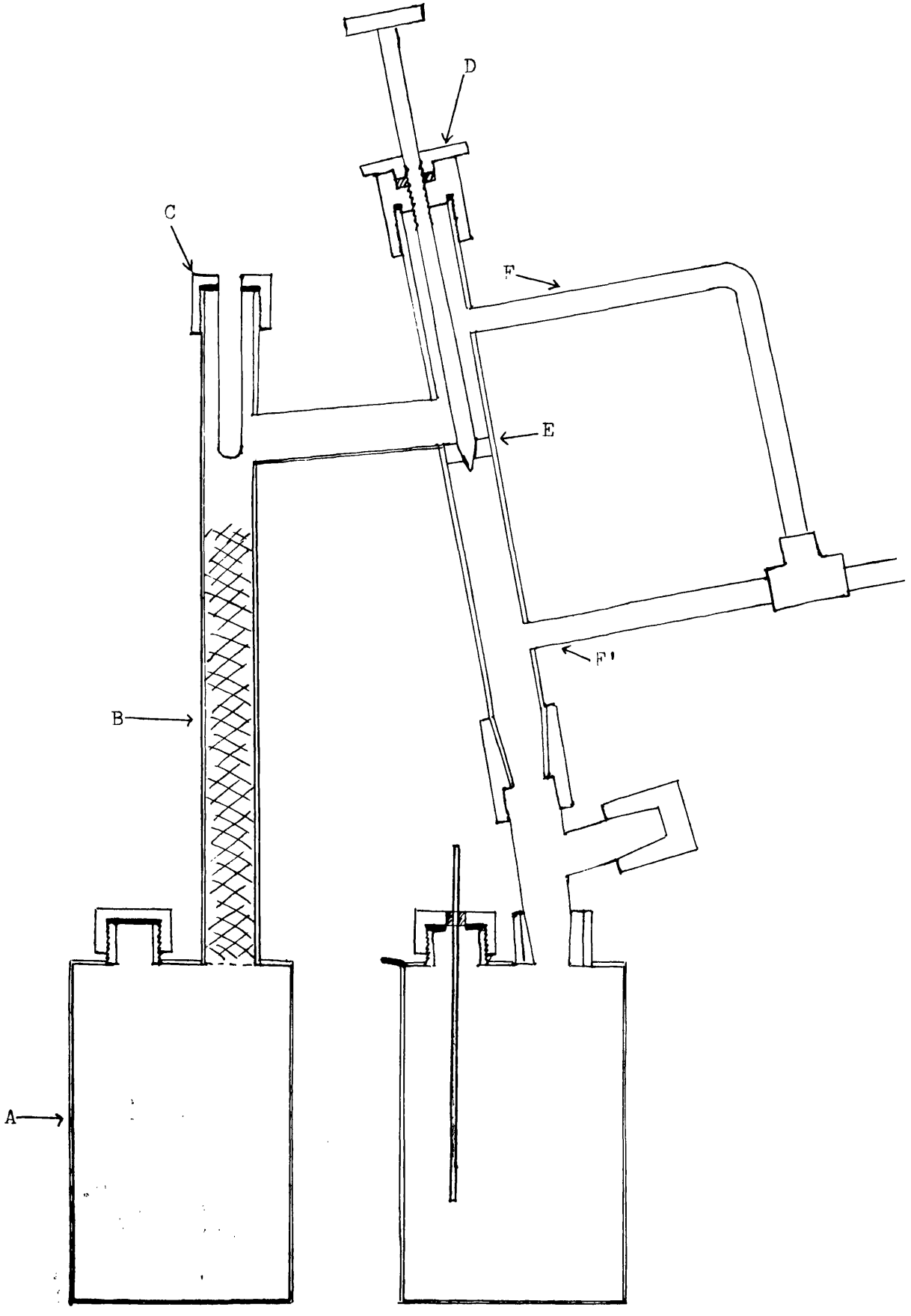

Fig. 9.

fluoride pellets. As only a maximum of 6.5 g. fluorine per hour was generated it was not possible to add bromine dropwise to the stream of fluorine, at the requisite rate. Instead the bromine container was immersed in a glycerol bath at 46-50° (V.P of Br_2 at 48° = 580 mm Hg and nitrogen was bubbled through to carry bromine vapour to a heated copper T-piece (80°) where it reacted with fluorine. The products of reaction were passed through a copper spiral in a water cooled copper receiver (300 ml. capacity) where they condensed out. The container was fitted with a condenser around the exit tube to prevent evaporation of bromine trifluoride in the stream of nitrogen. Approximately 90% yields of BrF_3 were obtained based on fluorine comsumption.

Bromine trifluoride was purified by distillation at atmospheric pressure in a nickel still, see diagram opp . It was relatively easy to separate bromine trifluoride (b.p. 126°) from the possible impurities, Br_2 (b.p. 59°), BrF (b.p. 23°), BrF_5 (b.p. 40°) and HF (b.p. 17°). The still consisted of a 220 ml. still pot (A) fitted with a screw cap and lead washer. The column (B) was packed with stainless steel helices (0.15 cm.) to a depth of 30 cm. The temperature at the column exit was measured in a nickel thermometer pocket (C). The rate of distillation was regulated by the adjustable screw (D) which fitted into the Teflon plug (E). The receiver arm was fitted with two copper side arms (F)(F^1) which were attached to sodium fluoride and alumina drying tubes. The depth of liquid in the receiver was measured using a nickel dip-stick, which fitted through a Teflon insulator in the cap. The dip-stick on contacting the liquid surface completed a circuit via the liquid, the nickel receiver, milliammeter and low voltage battery.

The fraction b.p. 125-127° was collected, straw-coloured bromine trifluoride being obtained indicating it was free of bromine and other low boiling impurities. Bromine trifluoride was stored in nickel containers before use.

Iodine pentafluoride was prepared by combination of the elements at room temperature. It was purified by vacuum distillation in silica and the colourless mid-fraction collected in thin walled glass ampoules. The purity of the product was confirmed by analysis.

Molybdenum powder (7-8 micron size) of reported 99.99% purity (Koch-Light) was heated in hydrogen at 1000° for a few hours to remove any traces of surface oxide. After this treatment molybdenum powder lost only 0.1% of its original weight. Spectrographic analysis gave Fe, 80; Al, 30; Ni, 10; Sn, 10; Cn, 1 and Mg, 1 p.p.m. as the only detectable impurities.

Potassium fluoride was prepared from pure potassium carbonate and hydrofluoric acid, and potassium fluorosulphate from potassium persulphate and bromine trifluoride[3], as described in Chapter III.

For reactions with bromine trifluoride, Analar bromine was distilled from phosphorus pentoxide into thin walled glass ampoules. Other solid reactants were finely ground, dried and stored over alumina.

Thermal equilibration of bromine trifluoride with bromine

Fluorination reactions with bromine trifluoride involve the liberation of bromine and the following equilibrium is established (a)

$$Br_2 + BrF_3 \rightleftharpoons 3BrF \qquad (a)$$

The generation of bromine monofluoride may affect the disproportionation of BrF_3 (b)

$$2BrF_3 \rightleftharpoons BrF_5 + BrF \qquad (b)$$

Before accurate thermal measurements can be made the heat of solution of bromine in bromine trifluoride has to be investigated. When bromine was added to pure bromine trifluoride there was an immediate rapid cooling effect presumably the heat of solution of bromine, and after one minute a slow heat evolution probably due to reactions (a) and (b). The heat of solution of bromine in pure bromine trifluoride and in bromine-bromine trifluoride solutions are given in Table I. The equilibration time is the time to reach steady Newtonian conditions after the additions of bromine.

TABLE I

Heat of solution of bromine in bromine trifluoride

Br_2 (g.)	BrF_3 (g.)	Initial weight Br_2 in BrF_3 (g.)	Mole ratio BrF_3/Br_2 Initial	Final	Equilibration* time (mins.)	Heat of solution (kcal./mole)
0.8609	315.6	0	-	428	14	-3.01
1.1417	264.8	0	-	271	17	-3.04
1.2737	308.4	0.86	419	169	14	-3.43
1.1830	312.9	0.83	439	182	23	-4.00
0.7162	303.1	2.03	180	129	20	-5.02
1.2352	300.0	2.73	129	88.8	29	-2.93
0.9228	333.0	15.5	25.1	23.7	5	-1.83
1.0489	361.8	16.4	25.8	24.2	5	-1.86

*Constant Newtonian conditions but not the anticipated Newtonian rates normally observed with the same temperature head

indicating that there was still a very slight heat evolution due to equilibria (a) and (b).

Because of

1) the above effect,

2) the equilibration times which were too long for accurate heat measurements by isothermal calorimetry,

3) the dependence upon solvent composition and history,

the heats of solution of bromine in more concentrated solutions of bromine in the trifluoride were examined. The amount of bromine required to initially saturate bromine trifluoride was measured and the solution was allowed to equilibrate. On standing the second phase dissolved. The amount of bromine required to saturate bromine trifluoride was determined by focusing a strong light on the trifluoride in a silica tube and adding bromine. The presence of drops of bromine in the mixture indicated that the solution was saturated initially. For the heats of solution (Table II), and for all subsequent measurements of fluorination reactions, 100 ml. of bromine trifluoride was mixed with 15.0 ml. of bromine and the mixture allowed to stand for at least two days to reach equilibration.

TABLE II

Heat of solution of bromine in bromine-bromine trifluoride solutions

Wt. Br_2 (g.)	Wt. BrF_3/Br_2 solution(g.)	BrF_3/Br_2 mole ratio Initial	Final	Heat of solution (kcal./mole)
1.3376	353.7	7.47	7.44	-0.54
1.5384	351.8	7.44	7.41	-0.70
2.4534	349.7	7.41	7.36	-0.75

Mean -0.66 ± 0.07

In all these experiments "correct" thermal equilibrium was attained within five minutes of introducing bromine. The mole ratio bromine trifluoride/bromine at saturation point has been reported as 4.64[15]. In all reactions involving the formation of bromine the mole ratios used in Table II were not usually exceeded except when reacting molybdenum with bromine-bromine trifluoride. In this reaction the BrF_3/Br_2 ratio drops to 6.6. If it is assumed that the, heat of solution of bromine in bromine saturated bromine trifluoride is zero and there is a linear heat of solution to BrF_3/Br_2, 7.47 when the heat of solution is -0.66 kcal./mole, then the heat of solution at BrF_3/Br_2 at the ratio 6.6 would be -0.46 kcal./mole. Hence error in the value for the heat of solution of bromine over the concentration range employed can be neglected within the limits of experimental error.

TABLE III

Heats of reaction in bromine-bromine trifluoride solutions.

Reactant	Wt. (g.)	Wt. BrF_3/Br_2 (g.)	Heat evolved per g. mole or atomic wt. (kcal.)
Mo	0.2047	31.3	213.3
	0.1938	23.7	214.3
	0.2044	33.2	213.8
	0.2334	36.2	214.2
		Mean 213.9 ± 0.3 (7)	
KIO_3	0.2677	441.3	94.18
	0.2751	437.6	94.61
	0.3015	434.6	94.62
		Mean 94.4 (4) ± 0.1 (8)	
K_2SO_4	0.6934	30.8	45.70
	0.7082	35.0	45.20
	0.7376	34.0	45.34
		Mean 45.4 (1) ± 0.2 (2)	
$K_2S_2O_8$	0.9290	23.4	55.89
	0.8757	32.7	55.32
	1.3626	24.4	54.45
		Mean 55.2 (2) ± 0.5 (1)	
KBr	0.3608	417.8	38.86
	0.2255	411.2	39.38
	0.2026	413.0	38.28
		Mean 38.84 ± 0.3 (7)	

Qualitative tests showed that no MoF_6 remained in the bromine-bromine trifluoride mixture after fluorination (see Appendix III).

TABLE IV

Heats of solution in bromine trifluoride solutions.

Solute	Wt. (g.)	Wt. BrF_3/Br_2 (g.)	Heat evolved per mole reacted (kcal.)
IF_5	1.1770	324.4	1.76
	1.1120	320.6	1.71
		Mean	1.73 ± 0.03
KF	0.2213	428.1	22.66
	0.2477	432.0	22.41
	0.2617	426.7	22.76
	0.3476	45.3[a]	22.87
	0.5479	33.2[a]	22.60
		Mean	22.6 (6) ± 0.12
KSO_3F	0.3822	53.5[a]	5.22
	0.4505	51.1[a]	5.34
	0.5286	46.2[a]	5.26
		Mean	5.27 ± 0.05

[a] Reaction carried out in "twin-cell" calorimeter.

Heat effect due to gas evolution.

When K_2SO_4, $K_2S_2O_8$, KIO_3 and Mo react with BrF_3 a gas is evolved. The heat effect cannot be accurately calculated because the vapour pressures and heats of vaporization of the species involved are not precisely known. This heat effect was measured by bubbling O_2 through Br_2 - BrF_3 solution (381.2 g.) in the calorimeter. A 250 ml. bulb of oxygen was immersed in the thermostat and the gas was displaced by mercury (250 ml./min.). The heat loss due to gas evolution was 2.52 ± 0.13 kcal./mole.

Auxiliary heats:-

The heats of formation of potassium iodate and potassium persulphate were needed in the final calculation and were redetermined. The heat of formation of KIO_3 was reported in Chapter II.

The heat of formation of potassium persulphate was found by measuring its heat of reaction with excess potassium iodide in dilute acetic acid[4], (30 g. KI + 250 ml. H_2O + 20 ml. 2N CH_3COOH). The reaction time, about 20 mins., was longer than desirable for isothermal environment calorimetry, but reasonable precision was achieved. Heat evolutions of 70.88, 70.16 and 70.50 kcal./mole were measured with additions of 0.6236, 0.6728 and 0.6221 g. of persulphate respectively (Mean 70.5 (5) ± 0.2 (5) kcal./mole). The heats of solution in the dilute acetic acid medium were assumed equal to those in water, (H_2O/CH_3COOH, mole ratio = 345).

Results

The auxiliary heats of formation used in the calculations, which differ from the N.B.S. Circular 500 values, are listed below:

1) $MoF_6(g)$ = -372.3 (5) ± 0.2 (2) kcal./mole[5]. This value was obtained by Hubbard et. al. by direct combination of the elements. In view of the incomplete reaction, MoF_5 formed and some Mo is unreacted, and the impurities of Mo_2C, Mo_3Si, MoO_2, Mo_2N and Mo_2S and their heats of fluorination; the error quoted seems to be slightly optimistic.

2) $HF2OH_2O$ = -77.0 hence HF gas = -65.5 kcal./mole. This value for HF has been reported by Sinke and Hubbard. However in view of the values listed in Chapter II there is still some doubt about the heat of formation of hydrogen fluoride.

3) KF = -136.1 kcal./mole. Revised with the new values of HF and KOH.

4) KSO_3F = -277.6 kcal./mole. (Chapter III)

5) H_2SO_4 = -194.6 kcal./mole. Reference(6)(7)

6) K_2SO_4 = -343.3 and K_2SO_4 $1000H_2O$ = -337.3 kcal./mole. Revised in light of new value for H_2SO_4.

7) KIO_3 = -119.7 kcal./mole. This is the mean of my value 119.9 ± 0.30 and that of Howard and Skinner[8] 119.5 ± 0.2. The latter value was calculated from the heat of reaction KIO_3 with aqueous hydrazine hydrochloride.

8) $K_2S_2O_8$ = -457.3 ± 0.4 (5) kcal./mole. This was the value obtained in this thesis from the heat of reaction

$$K_2S_2O_8 + 2KI = 2K_2SO_4 + I_2$$

9) $KI + I_2 + H_2O \rightarrow KI_{3aq}$ = -1.34 kcal./mole. Reference[9]

10) IF_5. This value has been obtained by Jeffes (Private communication) -211.0 ± 0.5. The value obtained from the heat of hydrolysis was -210.0 kcal./mole

$$IF_5 + 6KOH = 5KF + KIO_3 + 3H_2O$$

The value from the hydrolysis depends on 6KOH and KIO_3, with 5KF so the value obtained by combination of the elements is preferred.

11) $KOH(63H_2O)$ = -115.1 kcal./mole based on the new value for KOH. Reference[10]

12) KBr = -93.9 kcal./mole. Reference[11]

The heat of formation of the bromine-bromine trifluoride solution was obtained by substituting the appropriate heats of reaction in the following equations, where BrF_3 denotes the reactive species and the brackets indicate solution in the calorimetric liquid (Table V).

$$Mo + 2BrF_3 = MoF_{6(g)} + (Br_2)$$

$$3KBr + BrF_3 = 3(KF) + 2(Br_2)$$

$$KIO_3 + 2BrF_3 = (KF) + (IF_5) + (Br_2) + 1.5O_2$$

$$3K_2S_2O_8 + 2BrF_3 = 6(KSO_3F) + (Br_2) + 3O_2$$

$$2K_2SO_4 + 2BrF_3 = 3(KF) + 3(KSO_3F) + (Br_2) + 1.5O_2$$

TABLE V

Derived heats of formation of bromine-bromine trifluoride solution

Reactant	Products	-Dervied heat Br_2-BrF_3 (kcal.)
Mo	MoF_6, Br_2	77.6 ± 0.5
KIO_3	KF, IF_5, O_2	76.5 ± 0.7
KBr	KF, Br_2	76.8 ± 1.2
$K_2S_2O_8$	KSO_3F, O_2	75.6 ± 1.6
K_2SO_4	KF, KSO_3F, O_2	77.1 ± 1.0
	Mean*	76.9 ± 0.85

*Weighted according to mean deviations.

Discussion.

The composition of equilibrium mixtures of bromine fluorides and bromine has only been partially investigated and mainly in the gas phase. Bromine vapour equilibrated rapidly with gaseous bromine trifluoride at 25°. The pressure rise, indicated an equilibrium with a constant of approximately 0.1 which was calculated from manometric and spectrophotometric data[12].

$$Br_2 + BrF_3 \rightleftharpoons 3BrF \qquad (1)$$

The spectrum of the equilibrium mixture and a F:Br ratio of unity for the products gave further evidence for (1). Infra-red studies by Stein confirmed this equilibrium except that some pentafluoride was found in non equilibrium quantities[13]. The

presence of bromine pentafluoride was explained by partial disproportionation of the trifluoride (2)

$$2BrF_3 \rightleftharpoons BrF + BrF_5 \qquad (2)$$

It was found that gaseous bromine and bromine pentafluoride did not interact after 1 hour at 25°. At 150° they reacted at a "moderate rate" to form the lower bromine fluorides. It has been observed that both bromine monofluoride and bromine pentafluoride appear in bromine trifluoride after long storage at room temperature, suggesting that disproportionation of the trifluoride takes place very slowly. An approximate equilibrium constant of 10^{-4} for reaction (2) at 200° was found by spectrophotometric examination of the vapour quenched to room temperature and assuming no recombination of the products on rapid cooling. The constant can also be calculated as $10^{-6.7}$ at 25° from Stein's[14] free energy data and presumably the amount of pentafluoride usually present may well be less than indicated because of slow equilibration.

The detailed composition of the two liquid phases formed on mixing bromine with bromine trifluoride is not known. The ionic species can only be minor constituents from conductivity data[15]. The major constituents, in order of increasing volatility at 25° are BrF_3, Br_2, BrF_5 and BrF. Such a mixture would appear to be too complex for calorimetric measurements. However it can be used in practice because of the difference in reactivities between the bromine fluorides, and because of the low pentafluoride content. The amount of pentafluoride formed from equilibrium (2) is small, and because it is inversely related to the monofluoride content, it can be reduced even further by addition of bromine which generates more monofluoride

via equilibrium (1). The monofluoride and trifluoride remain the two possible reactive species in solution. Since bromine or bromides are displaced in reactions with bromine trifluoride and no stable adducts of the monofluoride are known, it is reasonable to assume that the trifluoride is the only calorimetrically reactive species. Pure bromine monofluoride has never been isolated[16]; its existence is deduced from equilibrium measurements and spectroscopic observation in the gas state.

In fluorination reactions with bromine trifluoride, bromine is liberated and its thermal influence upon equilibria (1) and (2) had to be measured. The heat of addition of bromine to bromine trifluoride was thoroughly examined. There was an initial cooling followed by a slow heat evolution when bromine was added to freshly distilled bromine trifluoride. Successive additions gave similar effects. Newtonian conditions were reached after 14 to 29 minutes, however the observed rates of cooling were lower than the anticipated rates. There was a slight but constant heat evolution probably due to equilibria (1) and (2). The heat change varied between -(2.9 to 5) kcal./mole of bromine and was not simply related to the quantity of bromine in solution. The error in the heat measured is probably due to "incorrect" Newtonian rates. Thus this system was unsatisfactory for accurate isothermal environment calorimetry. Hence bromine trifluoride was first equilibrated with an excess of bromine, sufficient to form initially a second phase but which on standing dissolved. The heat of addition of bromine to the equilibrated solution was then consistently small and quickly reached equilibrium. An undersaturated solution of bromine in

the trifluoride, (mole ratio BrF_3/Br_2 = 7.47) at 25° was adopted for thermal measurements[17]. It has additional advantages. The same liquid could be used in successive experiments provided the BrF_3/Br_2 ratio is within 6-8, the bromine pentafluoride content is suppressed to almost the maximum extent and the presence of bromine moderates the more vigorous reactions. An undersaturated solution was chosen as a compromise to reduce the vapour pressure above the liquid.

The heat of formation of the reactive species in this mixture was determined most directly by fluorinating molybdenum. This metal was selected because it is converted to the hexafluoride at 25° in bromine trifluoride without chemical interaction in solution[18]. The heat of formation of molybdenum hexafluoride has been determined recently by fluorine bomb calorimetry[5]. Under the experimental conditions all molybdenum was volatilized from the calorimeter as the hexafluoride and a correction for the heat effect due to gas evolution was included in the calculation of heat of formation.

A less direct route by reaction with potassium iodate involved the formation of iodine pentafluoride. It has been shown by Woolf that oxygen is displaced quantitatively and potassium tetrafluorobromate remains on removal of solvent[3]. Iodine pentafluoride is the only product from iodine and bromine trifluoride[19] and it has a small heat of solution. The heat of reaction of potassium iodate with bromine trifluoride added to the heat of alkaline hydrolysis of iodine pentafluoride gave a value for the bromine-bromine trifluoride mixture in terms of ΔH_f° of water, potassium fluoride and hydroxide.

$KIO_3 + 2BrF_3 = KF + IF_5 + Br_2 + 1.5O_2 + 74.5$ kcal.

$IF_5 + 6KOH_{H_2O} = 5KF + KIO_3 + 3H_2O + 104.7$ kcal.

Overall $2BrF_3 = 6KF + 3H_2O - 6KOH_{H_2O} + 179.2$ kcal.

when α- ΔH_f $Br_2/BrF_3 = 76.0$ kcal.

This differs from the value calculated from reaction of potassium iodate with bromine trifluoride because of the different values of ΔH_f for iodine pentafluoride. The values adopted for potassium fluoride and hydroxide are a major source of uncertainty in the derived value of the trifluoride. The values used are discussed in Chapter II. There is reasonable agreement between the heats of formation of "bromine trifluoride" derived via reactions with molybdenum and potassium iodate.

The least direct route for establishing the "bromine trifluoride" value was by converting potassium sulphate and persulphate to potassium fluorosulphate[3] the heat of formation of which have been determined in Chapter III. With potassium sulphate the measured heats of reaction were:

$3K_2SO_4 + 2BrF_3 = 3(KF) + 3(KSO_3F) + (Br_2) + 1.5O_2$

$K_2SO_4 + 2HSO_3F = 2(KSO_3F) + (H_2SO_4)$

from which the "bromine trifluoride" value was derived.

With potassium persulphate the measured reaction heats were:

$3K_2S_2O_8 + 2BrF_3 = 6(KSO_3F) + (Br_2) + 1.5O_2$

$K_2S_2O_8 + 2(KI) = 2(K_2SO_4) + 3(I_2)$ in water

In each of the four above methods a gas was evolved, either O_2 or MoF_6. This is a source of uncertainty and hence in the final method a reaction without gaseous products was chosen. Potassium bromide was converted to the tetrafluorobromate.

$3KBr + 4BrF_3 = 3(KBrF_4) + 2(Br_2)$

The value for "bromine trifluoride" obtained via the five

routes outlined (Table VI) is consistent within the limits of experimental error. The value for the molybdenum reaction, requiring fewest auxiliary data, would seem the best value but the heat correction is less certain. Hence a mean value is adopted. The heats of formation of iodine pentafluoride and potassium fluorosulphate that could be obtained using this value compare favourably with the heats derived from reactions in water or fluorosulphuric acid, or fluorine bomb calorimetry.

The reactive species in the bromine-bromine trifluoride mixture need not be specified for calorimetry but it seems likely that it is essentially bromine trifluoride, as previously discussed.

Operational use of bromine-bromine trifluoride solution in reaction calorimetry.

The mixture contains BrF_3, BrF and BrF_5 and when a heat is measured, it may be due to the following possible reactions (1), where M is a metal, oxide or salt.

(1) $M + \frac{n}{3} BrF_3 \longrightarrow MF_n + \frac{n}{6} Br_2 \qquad \Delta H_1$

or $M + n\ BrF \longrightarrow MF_n + \frac{n}{2} Br_2$

or $M + \frac{n}{5} BrF_5 \longrightarrow MF_n + \frac{n}{10} Br_2$

or a mixture of BrF_3, BrF and BrF_5. It has to be assumed that a constant proportion of the three bromine fluorides are engaged in reactions or only BrF_3, from indirect evidence.

To find the unknown heat of formation of M^1 the heat of reaction with bromine-bromine trifluoride solution is measured

(2) $M^1 + \frac{m}{3} BrF_3 \longrightarrow MF_m + \frac{m}{6} Br_2 \qquad \Delta H_2$

Then eliminate BrF_3 (or any appropriate mixture of bromine

fluorides) by substracting m x (1) from n x (2)

$$m\,M + \frac{mn}{3}\,BrF_3 \longrightarrow m\,MF_n + \frac{mn}{6}\,Br_2 + m\Delta H_1$$

$$n\,M^1 + \frac{mn}{3}\,BrF_3 \longrightarrow n\,M^1F_m + \frac{mn}{6}\,Br_2 + n\Delta H_2$$

$$m\,M - n\,M^1 \longrightarrow m\,MF_n - n\,M^1F_n + m\Delta H_1 - n\Delta H_2$$

A small heat of solution of Br_2 may be involved if M and M^1 are different types of compounds. Hence ΔH_f^{298} of M^1 is found in terms of ΔH_f^{298} of M, MF_n and M^1F or any one of the others in terms of the other three.

Hence whatever mixture is assumed in the equation, because it is eliminated when determining unknown heats, it is not necessary to specify it, provided of course that there is no selectivity in the reactivity of any component. This assumption is vindicated by consistent values for the heat of formation of bromine-bromine trifluoride mixture, obtained in a variety of reactions.

Even if some bromine pentafluoride were present in the equilibrium mixture it would not significantly affect the heat of formation of the trifluoride because its fluorinating power relative to bromine trifluoride (5:3) is balanced by approximately the same ratio (inversed) of formation heats[14]. The stability of bromine pentafluoride adducts in bromine-bromine trifluoride solutions has not been examined but from the relative ease of formation and stability of the adducts with alkali fluorides[20] it seems likely that bromine pentafluoride adducts would be solvolysed in bromine trifluoride. If this were true bromine pentafluoride would not be calorimetrically effective even if it reacted faster than the trifluoride in solution.

Two previous values have been reported for the heat of formation of bromine trifluoride.

The first was derived indirectly from the mean dissociation energy of bromine monofluoride obtained spectroscopically (61.1[21]; 60.6[22] and 65.5[23] kcal.) together with the heat of equilibration of bromine with bromine trifluoride (11.9 kcal.[12]) (3).

$$Br_{2(g)} + BrF_{3(g)} = 3BrF_{(g)} \qquad (3)$$

It is assumed that bromine monofluoride dissociates to a ground state bromine atom and an excited fluorine and that bromine pentafluoride is absent from the equilibration. Any errors in the dissociation energy of the monofluoride are magnified three-fold in the value for the trifluoride.

The second method was by direct combination of the elements[14]. The method is only superficially simple because of the non-equilibrium formation of some 5-10% BrF_5 at lower temperatures (25-44°). The composition of the fluorine, bromine trifluoride and pentafluoride mixture had to be determined in each experiment. The heat of formation of the pentafluoride was determined in separate experiments at 105-128°. Even at high temperatures using excess fluorine the reaction was slow (1 hour) and at 25° (2 hours); hence adiabatic calorimetry was used. The results had then to be corrected to 25° making assumptions about ideality of bromine fluorides and their mixtures. The three values are collected in Table VI.

TABLE VI

The heats of formation of liquid bromine trifluoride.

Method	Derived value (kcal./mole)
$BrF \rightarrow Br + F^*$)) $Br_2 + BrF_3 = 3BrF$)	79 ± 6
$Br_2 + F_2 \rightarrow BrF_5$)) $Br_2 + F_2 \rightarrow BrF_3; BrF_5; F_2$)	72.5 ± 0.8
See Table V	76.9^* (less heat of solution of Br_2 in 7.47 BrF_3)

*This value refers to the bromine trifluoride-bromine mixture and a value for pure BrF_3 can only be determined by measuring the heat of reaction of bromine with bromine trifluoride to form a mixture with the mole ratio, 7.47. When bromine is added to pure bromine trifluoride there is a slow heat evolution after a negative heat of solution. The heat evolution being extremely slow would be difficult to measure accurately but it indicates that the bromine-bromine trifluoride mixture has a higher heat of formation (more stable) than pure bromine trifluoride. This is shown by comparison with the more accurate value of Stein given above.

The feasibility of using a solution of bromine in bromine trifluoride for reaction calorimetry at 25° has been demonstrated by the consistency of values obtained for the heat of formation of the effective fluorinating entity in this solution. Further refinement of calorimeter design should increase precision but even at the present stage uncertainty in auxiliary data affects results as much as calorimetric error. Some applications of

bromine-bromine trifluoride solutions as a reaction medium for calorimetry are described in Chapter VI.

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CHAPTER V

THERMOCHEMISTRY OF IONIC REACTIONS IN BROMINE TRIFLUORIDE

Introduction

The high conductivity of bromine trifluoride has been attributed to the self ionisation[1][2]

$$2BrF_3 \rightleftharpoons BrF_2^+ \text{ and } BrF_4^-$$

and acids and bases containing these cations and anions respectively have been isolated. Ternary complexes were made by neutralisation reactions. The heats measured may provide information about the postulated ionic reaction mechanism in bromine trifluoride.

Materials.

Bromine trifluoride was prepared and purified as described in Chapter IV. Pure bromine trifluoride was used for most reactions except fluorinations when the mixture described previously (Chapter IV) was employed. Parent compounds for bases in bromine trifluoride: Fluorides of sodium, potassium, barium and lithium were prepared from the carbonates and 40% aqueous hydrogen fluoride. The fluoride was isolated then finely ground and stored over alumina. Qualitative tests proved the absence of carbonate and HF. Silver bromide prepared by mixing solutions of sodium bromide and silver nitrate, was dried at 110°. Parent compounds for acids in bromine trifluoride: Antimony pentafluoride (Ozark-Mahoning Company, Oklahoma) was purified by distillation under vacuum into thin-walled glass ampoules. There was no trace of oxide in the filled ampoules. Stannic fluoride: $SnCl_2 2H_2O$ was refluxed with acetic acid-acetic anhydride mixture for three hours, the solution was then cooled on ice, the precipitate filtered off, and washed (x 6) with ether. Bromine was added to $SnCl_2$ forming $SnCl_2Br_2$. Bromine trifluoride was

added and the excess removed in vacuo first at room temperature then at 250°. Tantalum pentafluoride (Ozark-Mahoning Company) was purified by fractional sublimation in vacuo.

Potassium tetrafluorobromate(III) was prepared from KF and BrF_3. Removal of excess solvent left a quantitative yield of white $KBrF_4$. The BrF_3 adducts of a) antimony and b) tantalum pentafluorides were prepared from a) Sb_2O_3 and BrF_3, b) TaF_5 and BrF_3; the excess solvent was removed and theoretical quantities of BrF_2SbF_6 and BrF_2TaF_6 obtained. An attempt to prepare the dibasic acid with stannic fluoride resulted in the formation of $SnF_4.1.2BrF_3$.

Sulphur trioxide and iodine pentafluoride were prepared as described in Chapter II. Molybdenum hexafluoride was prepared from the elements. Fluorine was passed over Mo powder in a Nickel dish in a 'Pyrex' glass container, the reaction being initiated by heat. MoF_6 was condensed into a trap (ethanol-'drikold'). The product was purified by distillation under vacuum in quartz apparatus. Colourless MoF_6 was collected in thin-walled glass ampoules.

Ternary complex fluorides were prepared by neutralisation reactions. Molar ratios of the parent acids and bases were treated with excess bromine trifluoride. The excess solvent was removed by vacuum distillation and theoretical quantities of ternary compounds were obtained.

Reactants + BrF_3	Product
NaCl, Sb_2O_3	$NaSbF_6$
AgBr, Sb_2O_3	$AgSbF_6$
KF, Sb_2O_3	$KSbF_6$
KF, TaF_5	$KTaF_6$
BaF_2, $SnCl_2$	$BaSnF_6$
KF, $SnCl_2$	K_2SnF_6
NaCl, $SnCl_2$	Na_2SnF_6

Calorimetry.

The heats of reaction of compounds forming bases in bromine trifluoride were measured (Table I). Pure bromine trifluoride was used for all measurements except with silver bromide when the bromine-bromine trifluoride mixture was used, (Chapter IV).

TABLE I

Heat of reaction of compounds forming bases in bromine trifluoride

Base	Wt. (g.)	Wt. BrF_3 (g.)	BrF_3/Base (mole ratio)	Heat reaction/mole base (kcal.)
	0.2383	416.2	739	21.76
KF	0.2159	414.6	811	21.96
	0.1922	418.1	922	22.21
			Mean	21.98 ± 0.16
	0.1953	424.5	667	12.07
NaF	0.2626	421.4	492	11.75
	0.3637	419.4	353	12.14
			Mean	11.99 ± 0.16
	0.3168	416.1	1680	21.16
BaF_2	0.3823	414.0	1380	21.23
			Mean	21.20 ± 0.04
	1.9458	36.5*	25.7	8.70
AgBr	1.8464	35.7*	27.0	8.59
			Mean	8.65 ± 0.06
	0.0757	409.0	276	2.79
LiF	0.5371	406.0	38.6	1.00**

* In twin-cell calorimeter

** Incomplete reaction, not all lithium fluoride dissolved.

TABLE II

The heat of solution of $KBrF_4$ in bromine trifluoride.

$KBrF_4$ (g.)	BrF_3 (g.)	$BrF_3/KBrF_4$ (mole ratio)	Heat per mole $KBrF_4$ dissolved (kcal.)
0.6184	412.8	951	- 0.37
0.7048	411.2	830	- 0.33
		Mean	-0.35 ± 0.02

The heats of solution of the basic adducts can be obtained from solubility data. For $KBrF_4$ this was calculated as -0.6 kcal./mole in reasonable agreement with the direct calorimetric value. Hence the other heats of solution were calculated from available solubility data[3].

The heats of reaction of compounds forming acids in bromine trifluoride were measured, Table III.

TABLE III

The heat of reaction of compounds forming acids in bromine trifluoride.

Compound	Compound (g.)	BrF_3 (g.)	BrF_3/Compound (mole ratio)	Heat/mole (kcal.)
	0.8088	357.4	700	21.94
SbF_5	1.1616	355.2	485	22.06
	1.1868	368.9	495	22.17
			Mean	22.06 ± 0.08
	3.5704	383.6	217	10.99
TaF_5	1.2160	380.1	628	10.60
			Mean	10.80 ± 0.20
	0.3663	415.8	1620	14.13
SnF_4	0.4219	411.2	1390	13.78
	0.3437	406.7	1680	14.22
			Mean	14.04 ± 0.18
	0.2392	363.4	887	21.36
SO_3	0.2532	353.2	815	21.00
			Mean	21.18 ± 0.18

TABLE IV

The heat of solution of BrF_2SbF_6 and BrF_2TaF_6 in bromine trifluoride.

Adduct	Wt. adduct (g.)	BrF_3 (g.)	BrF_3/Adduct (mole ratio)	Heat/mole adduct dissolved (kcal.)
BrF_2SbF_6	1.4398	369.4	662	1.19
	2.8280	367.8	490	1.17
			Mean	1.18 ± 0.01
BrF_2TaF_6	1.9394	413.0	642	0.32
	1.8678	411.2	663	0.35
			Mean	0.33 ± 0.02

As it was not possible to isolate pure $(BrF_2)_2SnF_6$, the heat of solution was estimated as approximately 0.5 kcal./mole.

TABLE V

Heat of solution of iodine pentafluoride and molybdenum hexafluoride in bromine trifluoride.

Fluoride	Wt. Fluoride (g.)	BrF_3 (g.)	BrF_3/Fluoride (mole ratio)	Heat/mole fluoride dissolved (kcal.)
MoF_6	0.8146	291.4	547	- 0.75
	0.9503	287.3	463	- 0.70
			Mean	-0.72 ± 0.03
IF_5	1.1770	324.4	445	1.76
	1.1120	320.6	469	1.71
			Mean	1.73 ± 0.03

TABLE VI

Heats of neutralisation in antimony pentafluoride-bromine trifluoride solution.

Base	Wt. Base (g.)	Wt. BrF_3 (g.)	Wt. SbF_5 (g.)	BrF_3/SbF_5/base (mole ratio)	Heat evolved per mole base neutralised (kcal.)
KF	0.1349	412.4	18.0	1300/36.0/1	26.29
	0.2100	408.0	17.5	1040/28.7/1	25.61
				Mean 25.95 ± 0.34	
AgBr	0.8008	439.6*	21.0	758/17.9/1	13.61
	1.3769	437.2*	20.0	600/12.6/1	12.89
				Mean 13.25 ± 0.36	
BaF_2	0.2235	364.8	14.5	2010/52.8/1.0	33.30
NaF	0.2161	416.1	15.0	590/13.4/1	12.17
	0.2369	413.2	14.0	565/11.5/1	11.91
	0.2237	411.0	12.8	565/11.2/1	12.02
				Mean 12.03 ± 0.10	
$KBrF_4$	1.7741	396.7	7.1	290/3.58/1	4.40
	1.5612	421.8	10.5	303/8.0/1	4.03
	1.8117	392.4	5.0	308/2.5/1	3.91
	2.1229	420.2	9.0	284/6.0/1	4.55
				Mean 4.23 ± 0.20**	

* Bromine-bromine trifluoride solution.

** May be slightly inaccurate due to difficulty in handling $KBrF_4$.

The heats of solution of ternary antimony complexes in bromine trifluoride were measured for silver and sodium, Table VII. The complexes of potassium and barium had only slight solubility in bromine trifluoride. Neutralisation reactions producing the

latter complexes were carried out in bromine trifluoride saturated with the complex.

TABLE VII

Heat of solution of ternary antimony complexes in bromine trifluoride.

Complex	Wt. Complex (g.)	Wt. BrF_3 (g.)	BrF_3/Complex (mole ratio)	Heat per mole complex dissolved (kcal.)
	0.4634	420.4	1,720	0.54
$NaSbF_6$	0.5155	417.2	1,530	0.51
	0.6529	414.9	1,190	0.40
			Mean	0.48 ± 0.05 kcal.
	0.6285	410.1	1,640	13.61
$AgSbF_6$	0.3936	412.6	2,620	13.42
	0.3892	406.9	2,630	13.18
			Mean	13.41 ± 0.15

The formation of precipitates in neutralisation reactions involving antimony pentafluoride, Table VI, may prevent complete reaction. Further heats of neutralisation were obtained by breaking antimony pentafluoride under various bases in bromine trifluoride (Table VIII).

TABLE VIII

Heat of reaction of antimony pentafluoride with various bases in bromine trifluoride.

Base in BrF_3	Wt. SbF_5 (g.)	Wt. BrF_3 (g.)	Wt. Base (g.)	BrF_3/Base/SbF_5 (mole ratio)	Heat evolved/ mole SbF_5 (kcal.)
$KBrF_4$	0.9600	324.4	4.1	530/15.8/1	26.76
	0.9640	320.0	3.2	522/12.2/1	26.65
				Mean	26.70 ± 0.06
$NaBrF_4$	0.8928	337.6	4.3	595/24.1/1	25.60
	1.3006	322.9	3.5	394/13.5/1	25.38
				Mean	25.49 ± 0.11
$AgBrF_4$	0.4727	296.7	1.4	1000/3.45/1	26.40
	1.4304	383.3	1.9	424/1.58/1	26.05
				Mean	26.22 ± 0.17
$Ba(BrF_4)_2$	0.5250	301.3	2.8	990/6.7/1	25.47
	0.6025	291.6	1.8	767/3.72/1	25.59
				Mean	25.53 ± 0.06

TABLE IX

Heats of neutralisation of various bases in stannic fluoride-bromine trifluoride solutions.

Base	Wt. Base (g.)	Wt. BrF_3 (g.)	Wt. SnF_4 (g.)	BrF_3/SnF_4/Base (mole ratio)	Heat/mole base neutralised (kcal,)
KF	0.1592	398.2	2.5	804/4.3/1	23.74
	0.2964	400.0	2.0	394/2.23/1	23.37
				Mean	23.55 ± 0.20
NaF	0.1147	388.2	2.6	1020/4.85/1	13.41
	0.1737	389.6	2.0	705/2.72/1	13.52
				Mean	13.46 ± 0.06

Table IX (contd..)

Base	Wt. Base (g.)	Wt. BrF_3 (g.)	Wt. SnF_4 (g.)	BrF_3/SnF_4/Base (mole ratio)	Heat/mole base neutralised (kcal.)
BaF_2	0.2142	382.8	1.5	2320/6.3/1	17.45
	0.5713	380.0	1.2	1080/2.4/1	17.72
				Mean	17.58 ± 0.13

TABLE X

Heat of solution of tin complexes in bromine trifluoride.

Complex	Wt. Complex (g.)	Wt. BrF_3 (g.)	BrF_3/complex (mole ratio)	Heat/mole (kcal.)
K_2SnF_6	0.5738	386.2	1,530	4.00
	0.7365	375.5	1,160	3.76
			Mean	3.88 ± 0.12
Na_2SnF_6	0.8777	390.8	1,190	2.58
	1.0923	388.2	710	2.41
			Mean	2.50 ± 0.09

TABLE XI

Heat of neutralisation of $KBrF_4$ in tantalum pentafluoride-bromine trifluoride solution.

Wt. $KBrF_4$ (g.)	Wt. BrF_3 (g.)	Wt. TaF_5 (g.)	$BrF_3/TaF_5/KbrF_4$ (mole ratio)	Heat/mole base neutralised (kcal.)
1.7868	394.0	6.7	303/2.65/1	3.14
1.5837	392.7	4.2	355/1.87/1	3.52
			Mean	3.33 ± 0.19

TABLE XII

Heat of solution of $KTaF_6$ in bromine trifluoride.

Wt. $KTaF_6$ (g.)	Wt. BrF_3 (g.)	$BrF_3/KTaF_6$ (mole ratio)	Heat/mole complex dissolved (kcal.)
0.5980	390.2	1,580	2.00
0.6101	387.7	1,530	1.58
		Mean	1.79 ± 0.21

TABLE XIII

Heat of neutralisation of KF with SO_3 in bromine trifluoride.

Wt. KF (g.)	Wt. BrF_3 (g.)	Wt. SO_3 (g.)	$BrF_3/SO_3/KF$ (mole ratio)	Heat/mole KF neutralised (kcal.)
0.1316	387.2	0.49	1250/2.7/1	20.44
0.1534	381.7	0.30	1060/1.4/1	22.50
			Mean	21.50 ± 1.0

Discussion

The high specific conductance of bromine trifluoride 8.0×10^{-3} ohm^{-1}cm.$^{-1}$[1][2] at 25°, cf ClF_3, 10^{-8}[4] and IF_5, 10^{-6} ohm^{-1}cm.$^{-1}$[5], was attributed to the following ionisation:

$$BrF_3 \rightleftharpoons BrF_2^+ + F^-$$

(The alternative ionisation BrF_2^- and F^+ is not energetically feasible). The small F^- ion can then be assumed to solvate,

$$F^- + BrF_3 \longrightarrow BrF_4^-$$

$$\text{overall} \qquad 2BrF_3 \rightleftharpoons BrF_4^- + BrF_2^+$$

The negative temperature coefficient of the conductivity of BrF_3 which is abnormal is attributed to the decrease in stability of BrF_2^+ and BrF_4^- ions at higher temperature.

It was found by Emeléus and Sharpe[2] that by reaction with BrF_3 some chlorides, bromides and iodides were converted to simple fluorides, but potassium, barium and silver halides formed the adducts $KF.BrF_3$, $AgFBrF_3$ and $BaF_2,2BrF_3$. The X-ray structures showed the absence of simple fluorides and of bromine trifluoride. The ratio of fluoride to bromine trifluoride was 1:1 for silver and potassium and 1:2 for barium. This indicated that the salts formed were $KBrF_4$, $AgBrF_4$ and $Ba(BrF_4)_2$ and that all three compounds contained the tetrafluorobromate(III) ion, (BrF_4^-). The existence of BrF_4^- was confirmed by Siegel[6][7] who determined the structure of $KBrF_4$ by X-ray diffraction. The solid is tetragonal with

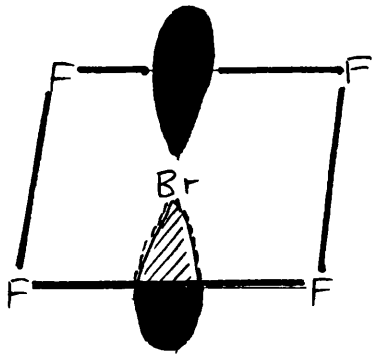
$$a = 6.162 \text{ k X}, \quad c = 11.081 \text{ k X and } Z = 4.$$

Similar lattice dimensions are given by Bouy[8]. Siegel reports a tetrahedral configuration for the ion and gives 1.81Å for the Br-F bond length. Sly and Marsh[9] indicate this structure is improbable, since the bromine may be expected to utilize sp^3d^2 hybrid orbitals. Reinterpreting the data they obtain a square planar configuration with Br-F = 1.88Å. The structure of BrF_4^- can only be resolved by having more accurate intensity measurements preferably from a single crystal. However BrF_4^- is most probably square planar because

1) The structure of $KICl_4$ shows a square planar ICl_4^- ion[10]

2) Isolectronic XeF_4[11] is square planar and

3) According to the lone pair repulsion theory the lone pairs would keep as far apart as possible to minimize repulsions.

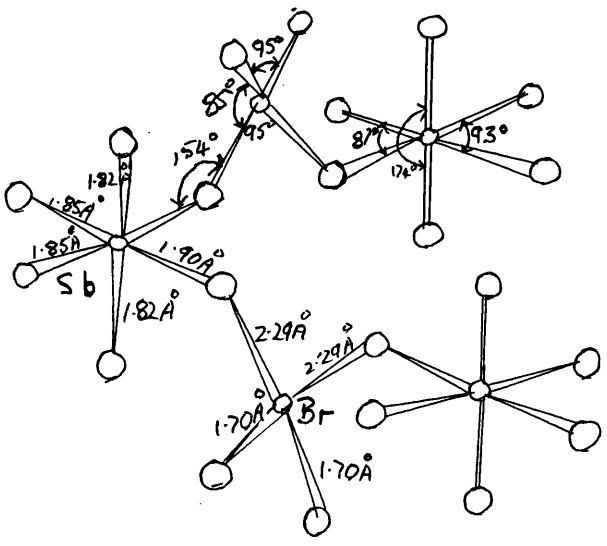


In similar experiments the adduct $SbF_5.BrF_3$ was formed which was ionised in bromine trifluoride, but not to form $SbF_4^+BrF_4^-$ since SbF_5 is a non-conductor and nearly always goes into anions e.g. SbF_6^- ion in alkali salts. This ionisation was confirmed by conductiometric titration with $AgBrF_4$ in bromine trifluoride[12].

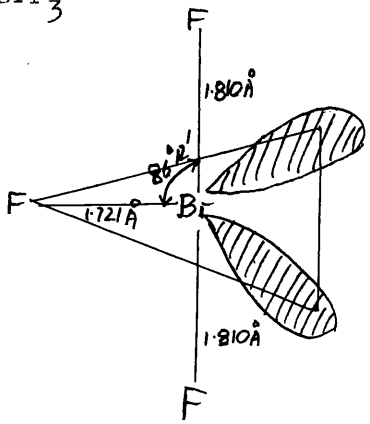
$$Ag^+BrF_4^- + BrF_2^+SbF_6^- = AgSbF_6 + 2BrF_3$$

The structure of $BrF_2^+SbF_6^-$ in the solid state has been determined recently by Edwards and Jones[13] who concluded that the adduct $SbF_5.BrF_3$ had molecular geometry consistent with weak fluorine bridging. The arrangement of the atoms is shown below:-

BrF_2SbF_6



BrF_3[14]

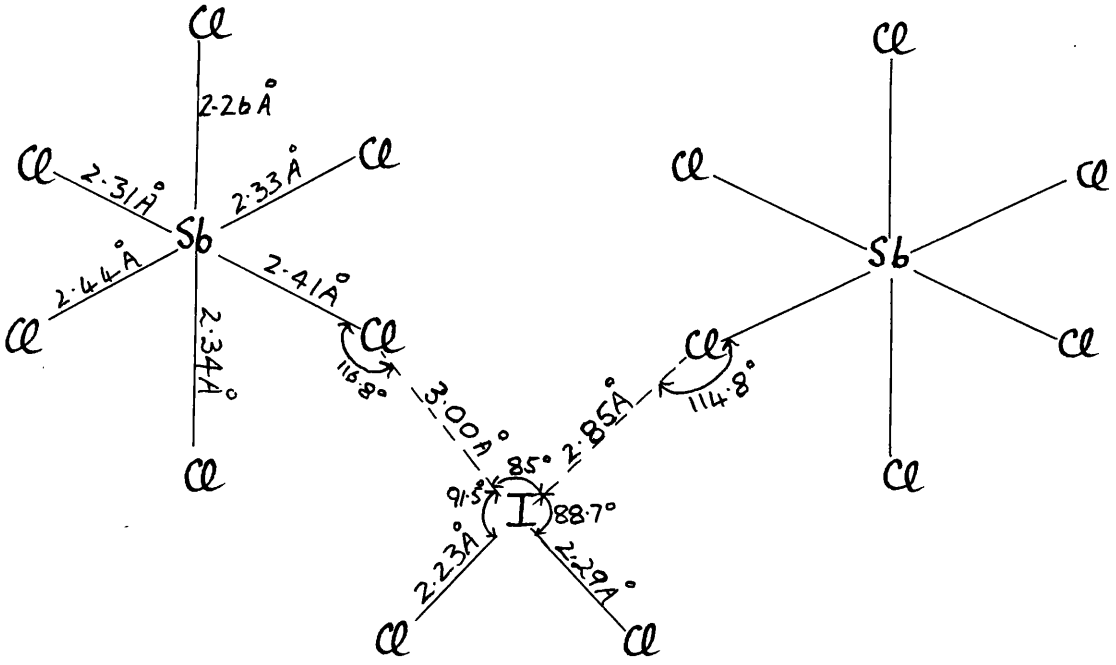


There is approximately octahedral coordination of the antimony atoms by fluorine atoms, with a slight distortion, shown by the length of the Sb-F bond nearest to the bromine atom, and by the terminal F-Sb-F bond angles of 93° and 174° rather than the expected 90° and 180°. The difference in length 0.06Å of the bridge from the terminal bonds is statistically just significant.

Although the bromine to fluorine bridge bond 2.29Å is considerably longer than the terminal bond (1.70Å) it is considered by Edwards and Jones to represent substantial interaction. This is supported by the two bridge fluorine atoms completing a distorted square plane around the bromine atom, as expected for covalent arrangement.

The structure can best be considered as predominantly derived from the ionic formulation $BrF_2^+SbF_6^-$ with some contribution from the covalent arrangement with a square planar BrF_4 unit linked through cis-bridging fluorine atoms to octahedral SbF_6 units to form endless chains. This solid structure is likely to lead to the formation of the ions BrF_2^+ and SbF_6^- on dissolution of the solid in liquid BrF_3 by breaking the weakest bridge bonds in agreement with conductivity data.

A similar structure was obtained for $ISbCl_8$[15], i.e. $ICl_2^+SbCl_6^-$. It is formed by combining $SbCl_5$ with ICl_3. This structure consists of angular ICl_2 and octahedral $SbCl_6$ groups but there is weak bonding in the groups which link them into chains. Each I forms two weak bonds (of length 2.9Å) in addition to those of (2.31Å) within the ICl_2^+ ion.



The I-Cl bridge bond is about 30% larger than that in the ICl_2 unit and the same relative extension holds in BrF_2SbF_6.

Emeléus and Woolf[12] using the terminology applied to other solvent systems such as water and ammonia classify as acids those compounds containing the cation BrF_2^+, (e.g.) $BrF_2^+SbF_6^-$ and as bases those compounds containing the anion BrF_4^-, (e.g.) $K^+BrF_4^-$.

<u>The effect of formation of an "acid" or "bases" in bromine trifluoride on the equilibrium $BrF_2^+ + BrF_4^- \rightleftharpoons 2BrF_3$</u>

Pure bromine trifluoride contains approximately 0.01 g. ions/ 1000 g. liquid of $BrF_2^+ + BrF_4^-$ due to the equilibrium (a)

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^- \qquad (a)$$

$K \simeq 10^{-4}$ where $K = [BrF_2^+][BrF_4^-] / [BrF_3]^2$

When potassium fluoride (0.003 mole) is added to BrF_3, BrF_4^- ions are formed.

$$KF + BrF_3 = K^+ + BrF_4^- \qquad (b)$$

The BrF_4^- ions (0.003 g. ion) may then suppress the ionisation (a). If all the BrF_4^- ions were consumed by suppressing (a) then the concentration of the anion would remain constant

(i.e.) 0.01 g. ion/1000 g. BrF_3

$$\overline{\angle BrF_4^- \angle} = \overline{\angle K^+ \angle} + \overline{\angle BrF_2^+ \angle}$$

This would give rise to a displacement of BrF_2^+ by less mobile K^+ ions and a decrease in conductivity would be expected on addition of KF to BrF_3. In fact the conductivity increases[12] indicating that equilibrium (a) is not greatly affected.

The heats of formation of acids and bases in bromine trifluoride are calculated on the assumption that the heat measured is due to formation of the acid or base and that the value obtained excludes any heat of neutralisation due to suppression of (a). The heat of neutralisation $BrF_2^+ + BrF_4^- \rightleftharpoons 2BrF_3$ is 4.50 ± 0.23 kcal. (see later).

Heats of formation of bases in bromine trifluoride

The heats of formation of $KBrF_4$, $NaBrF_4$, $Ba(BrF_4)_2$ were obtained by measuring the heat of reaction of the fluorides with pure bromine trifluoride. The value for $AgBrF_4$ was obtained by measuring the heat of reaction of silver bromide with bromine-bromine trifluoride solution (Chapter IV). Silver fluoride was not used because it is difficult to isolate.

The heat of solution of $KBrF_4$ in BrF_3 was determined experimentally, -0.33 kcal./mole which is slightly less than the value calculated from solubility data[3]. The difference in the values is probably due to the assumption that the heat of solution is constant over the temperature range of the solubility measurements (25-75°). The heat of solution was measured at 25°. There may also be a small error due to difficulty in

manipulating $KBrF_4$. Because it is difficult to manipulate the other bases, the calculated values from solubility data were used.

In Table XIV the heats of solution of the fluorides and their respective bases in bromine trifluoride are reported. These heats are combined with the heat of formation of pure liquid bromine trifluoride (-72.5 kcal./mole)[19] to obtain the heats of formation of the bases.

TABLE XIV

Fluoride	Product	Heat of solution (kcal./mole) Fluoride	Product	-Heat of formation of base (kcal./mole)
KF	$KBrF_4$	21.98 ± 0.16	-0.61	231.2
NaF	$NaBrF_4$	11.99 ± 0.16	-0.91	223.2
BaF_2	$Ba(BrF_4)_2$	21.20 ± 0.04	-2.25	397.1
AgF	$AgBrF_4$	10.4 ± 1.0[a]	-1.21	133.9
LiF	(b)	2.8 and 1.0	-	(b)

(a) This is calculated from the reaction

$$3AgBr + BrF_3 = 3AgF + 2Br_2$$

and the larger error is due to errors in the values for Br_2 - BrF_3, AgBr and AgF.

(b) Lithium fluoride has a small heat of solution and a low solubility in bromine trifluoride indicating that an extremely weak base is formed.

In Table XV the heats of solution of the fluorides in bromine trifluoride are compared with the equivalent conductivity of 0.01 g. mole/1000 g. BrF_3 solutions at 25°

TABLE XV

Base	Heat of solution kcal./mole	Equivalent Conductivity
KF	22.6	220[12]
AgF	11.7	207[12]
NaF	12.9	160[16]
BaF_2	23.4/2	114[12]

The four fluorides listed in Table XV have a high heat of solution in bromine trifluoride indicating that strong bases are formed but the base $KBrF_4$ is much stronger than the others. When the fluorides are dissolved in bromine trifluoride and the excess solvent is removed stoichiometric compounds can be isolated.

To date there is very little quantitative information on the stabilities of acids and bases in bromine trifluoride.

The dissociations to metal fluoride and halogen fluoride of $AgBrF_4$, $Ba(BrF_4)_2$ and $KBrF_4$ were compared by their relative reactivity with organic compounds, carbon tetrachloride, dioxan and acetone[2]. The silver and barium compounds were more reactive than the potassium salt.

Also the relative stabilities of $KBrF_4$ and $NaBrF_4$ can be shown by measuring the weight loss on heating at 200° for five minutes. $KBrF_4$ lost 30% of its weight whilst $NaBrF_4$ was completely decomposed to NaF and BrF_3[2].

The other quantitative method used to predict strengths of bases in bromine trifluoride was from conductivity data. The relative strengths from conductivity data are K > Ag > Na > Ba. From heat measurements it was found that K > Ag ≏ Na ≏ Ba.

Heats of formation of acids in bromine trifluoride

The heats of reaction of antimonic, tantalic and stannic fluorides and their respective acids with bromine trifluoride were measured. Combining these values with the heat of formation of pure bromine trifluoride (-72.5 kcal./mole)[19] the values for the acids were obtained.

TABLE XVI

Heats of formation of acids in bromine trifluoride

Fluoride	Heat of reaction with BrF_3 (kcal./mole)	Acid formed in BrF_3	Heat of solution of acid in BrF_3 (kcal./mole)	-Heat of formation of acid
SbF_5	22.06 ± 0.08	BrF_2SbF_6	1.18 ± 0.01	423.8[b]
TaF_5	10.80 ± 0.20	BrF_2TaF_6	0.33 ± 0.02	538.0[18]
SnF_4	14.04 ± 0.18	$(BrF_2)_2SnF_6$	0.5[a]	359.8[b]

[a] Estimated value $(BrF_2)_2SnF_6$ could not be isolated.

[b] See Chapter VI.

From the heats of reaction of the fluorides in bromine trifluoride the relative order of acid strength was Sb > Ta > Sn. Pure BrF_2SbF_6 and BrF_2TaF_6 were isolated from the fluoride and bromine trifluoride but when attempting to form $(BrF_2)_2SnF_6$ a non-stoichiometric product was obtained.

The phase diagram of SbF_5-BrF_3[17] system has been determined and it shows that four compounds exist.

$SbF_5.3.0BrF_3$)
) incongruently melting.
$SbF_5.1.5BrF_3$)

$SbF_5.1.0BrF_3$ m.p. 130°

$SbF_5.0.33BrF_3$ m.p. 35.5°

The 1:1 compound is the most stable and starting with an excess of the trifluoride it is the only one formed on removing the excess in vacuo. Equivalent conductivities at 0.01 molar were BrF_2SbF_6, 280 and ½$(BrF_2)_2SnF_6$, 155; cf. heat of reaction of fluoride in bromine trifluoride of 20.8 and 13.5 kcal./mole respectively.

The relative stabilities of the three acids were compared by heating BrF_2SbF_6[20], $(BrF_2)_2SnF_6$[20] and BrF_2TaF_6[21].

	Treatment	Moles of BrF_3 in residue
Sb	6 hours at 50°	1.00
	6 " " 110°	0.80
	4 " " 160°	0.72
	7 " " 160°	0.57
Sn	7 " " 15°	1.74
	7 " " 35°	0.75
	7 " " 100°	0.46
	7 " " 190°	0
Ta	6 " " 40°	1.00
	1 " " 100°	0.95
	1 " " 150°	0.80

Hence the relative stability of the acids was Sb > Ta > Sn which agrees with the heats of solution in bromine trifluoride.

The high heat of solution of sulphur trioxide is compatible with acid formation. Sulphur trioxide was reacted with bromine trifluoride and the excess BrF_3 removed in vacuo, a pale yellow liquid remaining. Analysis: %S = 14.6, F = 26.1, calculated for SO_3BrF_3, S = 14.8 and F = 26.3. The compound isolated was probably BrF_2SO_3F.

Iodine pentafluoride and molybdenum hexafluoride do not form acids in bromine trifluoride as indicated by their low heats of solution, 1.73 ± 0.03 and -0.72 ± 0.03 kcal./mole. They should not alter the conductivity of the solvent significantly.

Heats of neutralisation in bromine trifluoride

The dissolution of an acid or a base in bromine trifluoride causes the conductivity to increase. Titrations may be carried out between an acid and base in bromine trifluoride in which the end point corresponding to neutralisation is indicated by a sharp minimum in conductivity. Thus titrations of BrF_2SbF_6 and $(BrF_2)_2SnF_6$ with $KBrF_4$ in BrF_3 proceed as follows (1) and (2).

$$BrF_2SbF_6 + KBrF_4 = KSbF_6 + 2BrF_3 \qquad (1)$$

$$(BrF_2)_2SnF_6 + 2KBrF_4 = K_2SnF_6 + 4BrF_3 \qquad (2)$$

If there were no interaction the conductivity of the solutions would rise. (1) The initial conductivity is due to the ions K^+ and BrF_4^- together with those of the solvent, and the fall in conductivity as neutralisation is approached is due to the replacement of BrF_4^- by larger, less mobile SbF_6^- ion. On passing the equivalence point the conductivity rises because of the addition of BrF_2^+ and SbF_6^-. The equivalence point of the titration corresponded to $1KBrF_4:1BrF_2SbF_6$. In reaction (2) the end point corresponded to $2KBrF_4:1(BrF_2)_2SnF_6$. The complexes formed by these neutralisation reactions can be isolated by removal of excess solvent.

For strong acids and bases in bromine trifluoride a reasonably consistent value for the heat of neutralisation in bromine trifluoride should be obtained. However the values obtained may differ slightly from system to system due to

differences in concentrations of the solutions used and the degrees of solvolysis.

The values obtained using weaker acids and bases may be low due to solvolysis, which is the reverse of neutralisation, (i.e.) the combination of the acid and base is not complete and the complex formed from the neutralisation reaction is contaminated with bromine trifluoride when attempts are made to isolate it, (e.g.) $K_2SnF_6 0.95BrF_3$ [12]. Stannic fluoride forms only a weak acid in bromine trifluoride. When the acid is reacted with the strong base $KBrF_4$ the following reaction occurs,

$$2KBrF_4 + (BrF_2)_2SnF_6 \rightleftharpoons K_2SnF_6 + 4BrF_3$$

The combination of the acid and base is incomplete and the product isolated contained BrF_3 indicating it is a mixture of K_2SnF_6, $KBrF_4$ and $(BrF_2)_2SnF_6$. If solvolysis occurred the heat of neutralisation obtained would be expected to be less than that for a strong acid-strong base system. Ternary complexes isolated containing bromine trifluoride are $Ba(SbF_6)_2 \cdot 0.46BrF_3$ [20], $K_2TiF_6 \cdot 1.29BrF_3$ [20], $BaTaF_6 \cdot 0.09BrF_3$ [21], $Ag_2SnF_6 \cdot 0.27BrF_3$ [12] and $K_2SnF_6 \cdot 1.15BrF_3$ [20]. $BaSnF_6$ was isolated pure because it was insoluble in bromine trifluoride which prevents solvolysis.

The heats of neutralisation measured are listed in Table XVII.

TABLE XVII

Heats of neutralisation in bromine trifluoride

Acid (A)	Base (B)	Complex formed	BrF_3/Complex (mole ratio)	Heat of neutralisation $BBrF_3 + BrF_2A = AB_{BrF_3} + 2BrF_3$
SbF_5 in BrF_3	KF	$KSbF_6$	1040, 1300.	3.97 ± 0.37
SbF_5 in BrF_3	AgBr*	$AgSbF_6$	600, 758.	4.60 ± 0.32
SbF_5 in BrF_3	NaF	$NaSbF_6$	590, 565, 565.	0.04
SbF_5 in BrF_3	$KBrF_4$	$KSbF_6$	290, 303, 308, 284.	4.56 ± 0.24
SbF_5	KF in BrF_3	$KSbF_6$	522, 530.	4.63 ± 0.12
SbF_5	NaF in BrF_3	$NaSbF_6$	595, 394.	3.43 ± 0.13
SbF_5	AgF in BrF_3	$AgSbF_6$	1000, 424.	4.16 ± 0.20
SbF_5	BaF_2 in BrF_3	$Ba(SbF_6)_2$	990, 767.	3.50 ± 0.10
SnF_4 in BrF_3	KF	K_2SnF_6	804, 394.	1.55 ± 0.26
SnF_4 in BrF_3	NaF	Na_2SnF_6	1020, 705.	1.47 ± 0.17
SnF_4 in BrF_3	BaF_2	$BaSnF_6$	2320, 1080.	-2.64 ± 0.15
TaF_5 in BrF_3	$KBrF_4$	$KTaF_6$	303, 355.	3.66 ± 0.20

*Reaction carried out in bromine-bromine trifluoride solution.

a) Heat of neutralisation of BrF_2SbF_6 by a series of bases in bromine trifluoride

Antimony pentafluoride dissolves in bromine trifluoride to form a strong acid BrF_2SbF_6. This acid in bromine trifluoride was then neutralised by a series of bases, KF, NaF, AgBr and BaF_2. For reaction of BrF_2SbF_6 with AgBr the bromine-bromine trifluoride mixture (Chapter IV) was used. $KSbF_6$, $NaSbF_6$ and

$Ba(SbF_6)_2$ have limited solubility in bromine trifluoride, and the heats of neutralisation obtained may be variable and low due to incomplete reaction. $AgSbF_6$ is soluble in bromine trifluoride so the value obtained for the heat of neutralisation (1) should be accurate.

$$AgBrF_4 + BrF_2SbF_6 = AgSbF_6 + 2BrF_3 \qquad (1)$$

The heat of neutralisation was 4.56 ± 0.24 kcal./mole. Because precipitation of the complex may prevent complete reaction further heats of neutralisation were obtained by breaking ampoules of antimony pentafluoride under various bases in bromine trifluoride. The values obtained for the heat of neutralisation of $KBrF_4$, $AgBrF_4$, $NaBrF_4$ and $Ba(BrF_4)_2$ were 4.63, 4.16, 3.50 and 3.43 kcal./mole respectively. The low values obtained for $NaBrF_4$ and $Ba(BrF_4)_2$ could be due to slight solvolysis (2).

$$Ba(BrF_4)_2 + 2BrF_2SbF_6 \rightleftharpoons BaSbF_6 + 4BrF_3 \qquad (2)$$

$BaSbF_6.0.46BrF_3$ [20] has been isolated indicating that solvolysis had occurred.

b) Heats of neutralisation of $(BrF_2)_2SnF_6$ by a series of bases in bromine trifluoride

Heats of neutralisation in bromine trifluoride of $(BrF_2)_2SnF_6$ with KF, NaF and BaF_2 were measured. The values obtained were much lower than those obtained in SbF_5 - BrF_3 solutions. $(BrF_2)_2SnF_6$ is a much weaker acid than BrF_2SbF_6 and the low values obtained were probably due to solvolysis which prevents complete reaction. The evidence for solvolysis was that the hexafluorostannates isolated were contaminated with BrF_3, (e.g.) $K_2SnF_6.1.15BrF_3$ [20] and $Ag_2SnF_6.0.27BrF_3$ [20]. The pure barium salt has been isolated because it is insoluble.

If the reaction of BaF_2 with $(BrF_2)_2SnF_6$ went to completion then a value of 3-4 kcal./mole would be anticipated for the heat of neutralisation. The value obtained was -2.64 kcal./mole indicating that insoluble $BaSnF_6$ had formed on unreacted BaF_2 preventing complete reaction.

c) Heat of neutralisation of $KBrF_4$ with BrF_2TaF_6 in bromine trifluoride

BrF_2TaF_6 is a stronger acid than $(BrF_2)_2SnF_6$ but weaker than BrF_2SbF_6. An intermediate value was obtained for the heat of neutralisation, 3.66 kcal./mole which again could indicate a slight solvolysis.

$$KBrF_4 + BrF_2TaF_6 \rightleftharpoons KTaF_6 + 2BrF_3$$

Complexes isolated from TaF_5-BrF_3 contain small amounts of bromine trifluoride, (e.g.) $Ba(TaF_6)_2 0.09BrF_3$ [21].

The heats of formation of ternary complexes by neutralisation reactions in bromine trifluoride

These values were obtained from heats of neutralisation in bromine trifluoride. If solvolysis occurs incorrect heats of formation of the ternary fluorides will be obtained. Hence the value 4.50 kcal. is assumed for the heat of neutralisation.

TABLE XVIII

Heats of formation of ternary fluorides.

Acid	Base	Typical product composition	-Heat of formation of ternary fluoride (kcal./mole)
BrF_2SbF_6	$KBrF_4$	$KSbF_6$	512.1
BrF_2SbF_6	$AgBrF_4$	$AgSbF_6$	402.8
BrF_2SbF_6	$NaBrF_4$	$NaSbF_6$	504.3
BrF_2SbF_6	$Ba(BrF_4)_2$	$Ba(SbF_6)_2 0.46BrF_3$	1019.8
$(BrF_2)_2SnF_6$	$KBrF_4$	$K_2SnF_6 1.15BrF_3$	604.3
$(BrF_2)_2SnF_6$	$AgBrF_4$	$Ag_2SnF_6 0.27BrF_3$	495.2*
$(BrF_2)_2SnF_6$	$NaBrF_4$	Na_2SnF_6	591.1
$(BrF_2)_2SnF_6$	$Ba(BrF_4)_2$	$BaSnF_6$	597.3
BrF_2TaF_6	$KBrF_4$	$KTaF_6$	627.4
BrF_2TaF_6	$AgBrF_4$	$AgTaF_6$	530.5*
BrF_2TaF_6	$NaBrF_4$	$NaTaF_6$	620.1*
BrF_2TaF_6	$Ba(BrF_4)_2$	$Ba(TaF_6)_2 0.09BrF_3$	1250.4*

*The heat of formation obtained includes a small heat of solution of complex in bromine trifluoride.

Combining the heat of neutralisation of SO_3 in BrF_3 with the heats of solution of KF, SO_3 and KSO_3F a heat of formation of -278.8 ± 1.5 kcal./mole is obtained for KSO_3F. This compares favourably with the value obtained in Chapter III of -277.6 kcal./mole.

Heat of autoprotolysis of bromine trifluoride

From the heat of neutralisation a value for the heat of autoprotolysis of bromine trifluoride was obtained.

$$BrF_2^+ + BrF_4^- \rightleftharpoons 2BrF_3$$

The heats of neutralisation selected were those involving the

strong acid BrF_2SbF_6 with the bases $KBrF_4$ and $AgBrF_4$. The values obtained were 4.56 ± 0.24, 4.63 ± 0.12, 4.60 ± 0.32 and 4.16 ± 0.20, mean 4.50 ± 0.23 kcal./mole.

Both the equilibrium constant K and the specific conductivity depend upon the number of ions in the solvent.

$$-\Delta G^{\circ} = RT\ln K \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

for a reaction $\underset{(1-n)}{MX} + \underset{(1-n)}{MX} \rightleftharpoons \underset{n}{M^+} + \underset{n}{MX_2^-}$

where n:- number of ions.

$$K = {}^{n^2}/_{(1-n)^2}$$

if n is small, $K = n^2$ .. .. (2)

from equation (1) $K = e^{-\Delta G/RT} = e^{-(\Delta H - T\Delta S)/RT} \propto n^2$

The specific conductivity $= n\lambda_{M^+} + n\lambda_{MX_2^-}$

$$= n(\lambda_{M^+} + \lambda_{MX_2^-})$$

$\lambda_{M^+} + \lambda_{MX_2^-}$ are the mobilities of the ions.

Assuming the mobilities of the ions approximately constant for each system the spec. cond. $\propto$ n

and (spec. cond.)$^2 \propto n^2 \propto K \propto e^{-\Delta G/RT}$

then -log (spec. cond.) $\propto \Delta G$

The free energy, enthalpy and entropy changes of auto-protolysis and the specific conductivity (K) of several solvents are listed below.

	Solvent	ΔG (kcal.)	ΔH (kcal.)	$-\Delta S$ (cal./deg.)
a[1])	H_2SO_4 (25°)	7.50	5.0	8.4
a[2])		8.36	4.6[22]	11.9
b)	D_2SO_4 (25°)	10.43		
c)	BrF_3 (25°)		4.5	
d)	HSO_3F (25°)	12.35		
e)	HF (10°)	17.8	11.2[23]	23.2
f)	CH_3COOH (25°)	22.0	12.2	32.7
g)	H_2O (25°)	23.8	13.5	34.6
h)	NH_3 (-33°)	45.6	26.1[24]	75.0

	Solvent	$K_{ohm^{-1}cm.^{-1}}$	$-\log_{10}K$	$-\Delta G/\log K$
a[1])	H_2SO_4 (25°)	1.0×10^{-2}	2.0	3.75
a[2])		1.0×10^{-2}	2.0	4.18
b)	D_2SO_4 (25°)	2.6×10^{-3}	2.6	4.0
c)	BrF_3 (25°)	8×10^{-3}	2.1	
d)	HSO_3F (25°)	1.1×10^{-4}	4.0	3.10
e)	HF (10°)	1.0×10^{-6}	6.0	2.97
f)	CH_3COOH (25°)	4.0×10^{-9}	8.4	2.6
g)	H_2O (25°)	5.5×10^{-8}	7.3	3.3
h)	NH_3 (-33°)	1.0×10^{-11}[26]	11	4.1

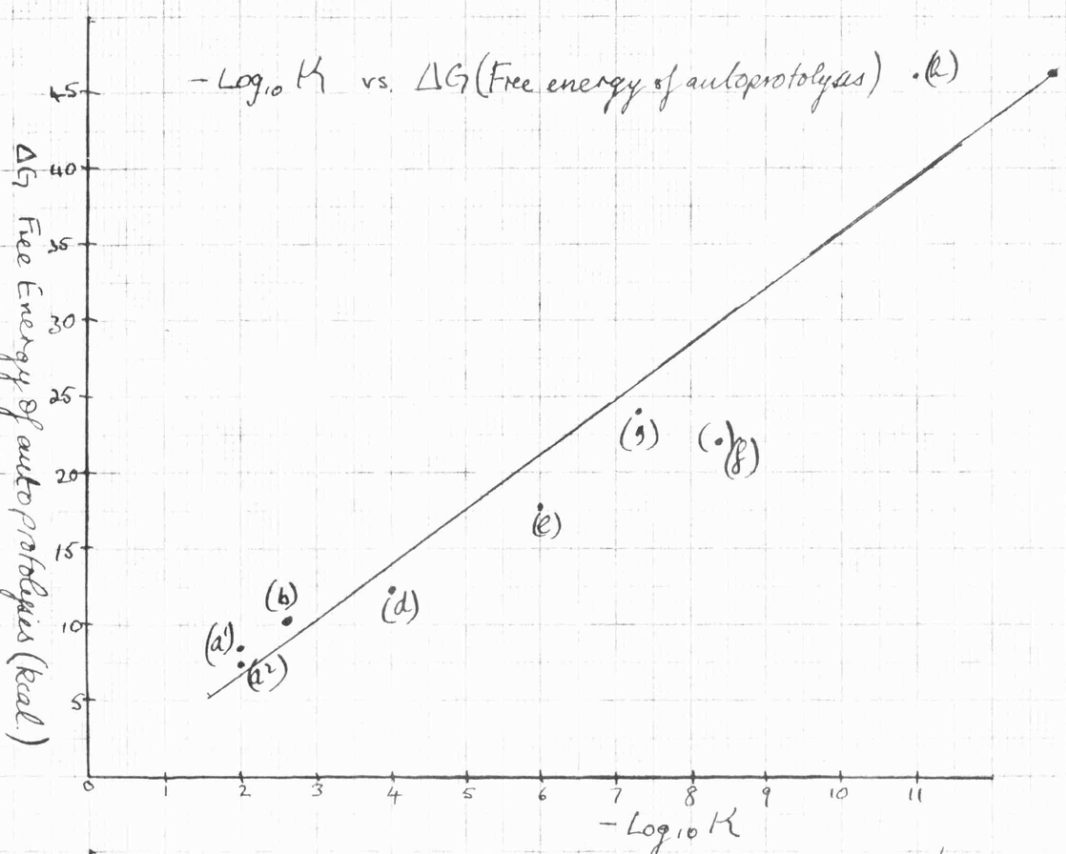
$\frac{-\Delta G}{\log K}$: Mean 3.4 ± 0.6

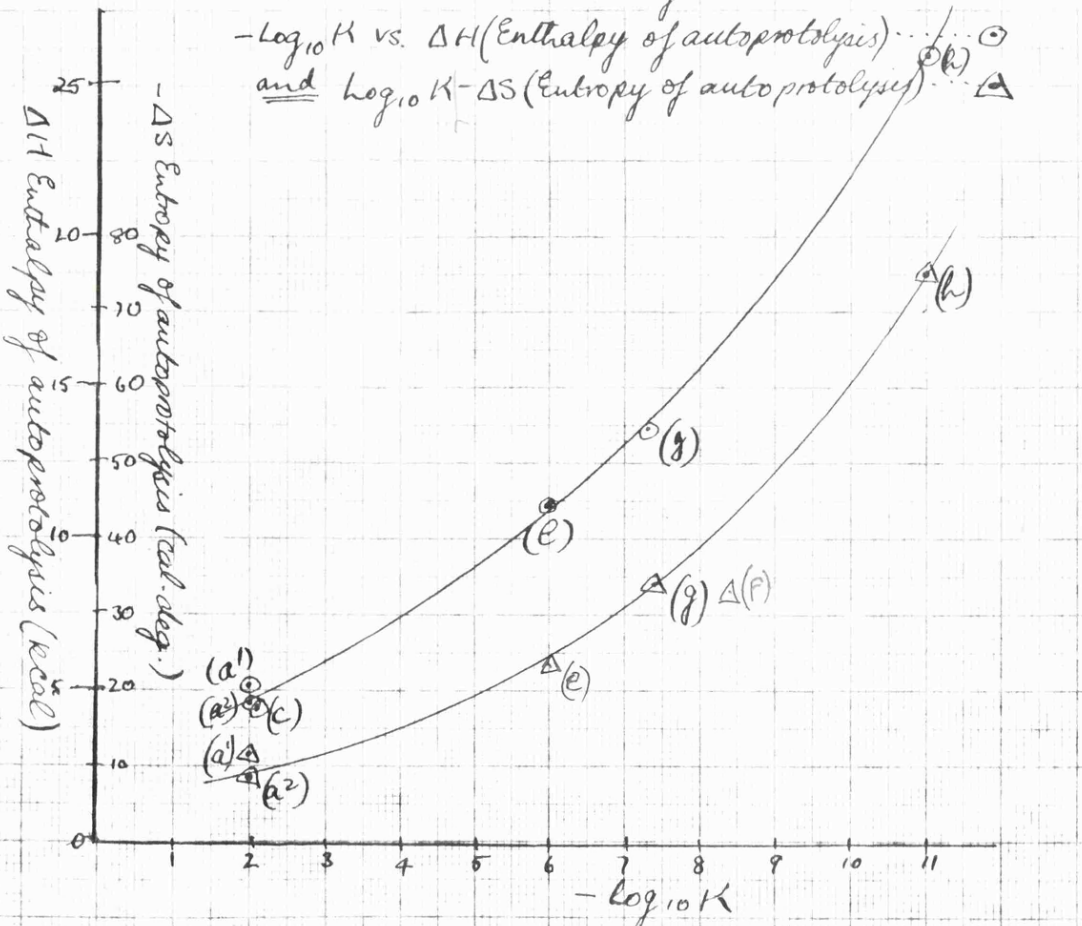
* 3.6 ± 0.5

*Except acetic acid.

Only acetic acid has a low dielectric constant and all solvents except BrF_3 are prototropic.

e) The enthalpy change for hydrogen fluoride was obtained from data reported by Mackor et. al.[23] who measured the heats of reaction:-


$-\log_{10} K$ vs. ΔG (Free energy of autoprotolysis)
ΔG Free Energy of autoprotolysis (kcal.)
$-\log_{10} K$
(a¹)
(a²)
(b)
(c)
(d)
(e)
(f)
(g)
(h)


$-\log_{10} K$ vs. ΔH (Enthalpy of autoprotolysis)
and $\log_{10} K - \Delta S$ (Entropy of autoprotolysis)
ΔH Enthalpy of autoprotolysis (kcal)
$-\Delta S$ Entropy of autoprotolysis (cal. deg.)
$-\log_{10} K$
(a¹)
(a²)
(b)
(c)
(d)
(e)
(f)
(g)
(h)

BF_3 (gaseous) + F^-(HF) = BF_4^-(HF) + 15.1 kcal./mole BF_3

BF_3 (gaseous) = BF_3(HF) + 3.9 kcal./mole BF_3

BF_3 acts as an acid in HF so the overall reaction is

$H^+BF_4^-$(in HF) + F^-(in HF) = HF + BF_4^- + 11.2 kcal.

f) The heat of autoprotolysis of acetic acid was obtained from the heat of reaction of potassium acetate with fluorosulphuric acid in glacial acetic acid (Chapter III)

$$HSO_3F + K(CH_3CO_2) \rightleftharpoons KSO_3F\downarrow + CH_3CO_2H$$

hence $H^+ + CH_3CO_2^- \rightleftharpoons CH_3CO_2H$ + 12.2 ± 0.3 kcal.

The graph of -log(K) vs. ΔH, ΔG and ΔS was plotted for the solvents listed, see opposite, and a value for BrF_3 obtained by interpolation.

ΔG_{BrF_3} = 3.6 x 2.1 = 7.55 ± 1.05 kcal. (from graph)

$-\Delta S$ = 9.9 ± 3.5 cal./deg. (Experimental ΔH)

The value for $-\Delta S$ from the graph is 10.0 cal./deg.

It has been suggested that the high conductivity of bromine trifluoride was due to impurity. However the value obtained for the heat of neutralisation is in good agreement with the conductivity value indicating that the high conductivity is most probably an intrinsic property.

The heats of autoprotolysis of other solvents can be estimated provided their conductivity is known, e.g. HSO_3F conductivity 1.1 x 10^{-4} $ohm^{-1}cm.^{-1}$ should have a heat of neutralisation of approximately 7.5 kcal. The heats of formation of carbonium ions in SbF_5-HSO_3F mixture have been measured[25] but to obtain a heat of neutralisation from this data the heats of solution of the organic compounds used in fluorosulphuric acid have to be measured.

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CHAPTER VI

APPLICATIONS OF BROMINE-BROMINE TRIFLUORIDE MIXTURE AS A REACTION CALORIMETRIC LIQUID

The heats of formation of antimony pentafluoride and stannic fluoride were obtained by reacting the metals with bromine-bromine trifluoride mixture in the "twin-cell" calorimeter. The values were required to obtain the heats of formation of a number of ternary complexes by neutralisation reactions in bromine trifluoride. (See Chapter V)

1. Heat of formation of antimony pentafluoride

Wt. Sb (g.)	Wt. Br_2-BrF_3 solution (g.)	BrF_3/Sb (mole ratio)	Heat evolved/g. atom of Sb (kcal.)
0.2850	36.0	114	223.3
0.1955	32.1	148	222.7
0.3033	23.0	68	224.6
0.2420	27.0	100	220.5

Mean 222.8 ± 1.2

Combining the above heat of reaction with the heat of formation of Br_2-BrF_3, -76.9 kcal./mole the heat of formation of SbF_5 is obtained.

$$3Sb + 5BrF_3 = 3SbF_5 + 2.5Br_2 \text{ in } Br_2\text{-}BrF_3$$

$$-\Delta H_f\ SbF_{5BrF_3} = 351.5 \text{ hence } -\Delta H_f\ SbF_5 = 329.5 \pm 1.5 \text{ kcal./mole}$$

2. Heat of formation of stannic fluoride

$$3Sn + 4BrF_3 = 3SnF_4 + 2Br_2 \text{ in } Br_2\text{-}BrF_3$$

Wt. Sn (g.)	Wt. Br_2-BrF_3 solution (g.)	BrF_3/Sn (mole ratio)	Heat evolved/g. atom of Sn (kcal.)
0.2643	41.1	135	183.0
0.2541	29.7	101	181.4
0.1702	21.3	109	182.5

Mean 182.3 ± 0.6

Combining the above heat with the heat of formation of Br_2-BrF_3 and the heat of solution of SnF_4 in BrF_3, $-\Delta H_f$ SnF_4 = 271.5 ± 1.1 kcal./mole.

It was found by empirical observation (Chapter III) that some fluorides have similar heats of formation to the corresponding hydroxy compounds. The value for SnF_4 (-271.5 kcal./mole) seems a reasonable value because it is approximately the same as $Sn(OH)_4$(-275 kcal./mole) or $SnO_2 + 2H_2O$(-274 kcal.)

3. Heat of formation of $SeOF_2$

The sample was prepared and purified by M. J. Stiff[1]. It was prepared by the action of fluorine on selenium dioxide[2] and purified by distillation under vacuum. He attempted to measure the heat of formation by alkaline hydrolysis but was unsuccessful because of slow reaction and mixed products. The reaction with BrF_3 seemed a reasonable alternative. The heat of formation of $SeOF_2$ was obtained by measuring the heat of reaction with Br_2-BrF_3 mixture in the nickel-plated brass calorimeter.

$$3SeOF_2 + 4BrF_3 = 3SeF_6 + 1.5O_2 + 2Br_2$$

SeF_6 is a gas and escapes from the Br_2-BrF_3 mixture.

Wt. $SeOF_2$ (g.)	Wt. BrF_3/Br (g.)	$BrF_3/SeOF_2$ (mole ratio)	Heat of reaction/mole $SeOF_2$ (kcal.)
0.7855	369.4	457	14.71
0.7248	361.8	482	15.20
		Mean	14.96 ± 0.25

Combining the heat of reaction with the heat of formation of Br_2-BrF_3 mixture (-76.9 kcal./mole) and $SeF_{6(g)}$ = -266.9 kcal./mole[6], the heat of formation of $SeOF_2$ = -147.6 kcal./mole.

The anticipated value was approximately -126 kcal./mole, i.e. the heat of formation of $SeO(OH)_2$, selenious acid.

The value obtained may be in error because the sample supplied had not been analysed and may contain SeF_4 which is difficult to separate from $SeOF_2$ by distillation as they have similar boiling points, 106° and 124° respectively. Although the determination needs repeating with authenticated material, the principle of the method has been established.

4. Heats of formation of monoclinic and orthorhombic stannous fluoride

The heats of formation of the two forms of stannous fluoride were obtained by measuring the heat of reaction with Br_2-BrF_3 mixture forming stannic fluoride. The two forms were prepared and supplied by J. D. Donaldson[3] who first isolated the orthorhombic form by evaporating solutions containing high concentrations of tin(II) fluorides with other metal(II) fluorides. Tin(II) fluoride normally crystallizes in the monoclinic form.

a) Monoclinic SnF_2

Wt. SnF_2 (g.)	Wt. Br_2/BrF_3 (g.)	BrF_3/SnF_2 (mole ratio)	Heat evolved/mole SnF_2 (kcal.)
0.1620	452.9	3,220	112.3
0.1904	447.2	2,690	110.2
0.2006	440.7	2,530	110.9

Mean 111.2 ± 0.7

b) Orthorhombic SnF_2

Wt. SnF_2 (g.)	Wt. Br_2/BrF_3 (g.)	BrF_3/SnF_2 (mole ratio)	Heat evolved/mole SnF_2 (kcal.)
0.1778	431.2	2,780	129.6
0.1567	424.6	3,100	128.4
0.1545	418.0	3,110	129.8
		Mean	129.3 ± 0.6

Combining the heats of reaction with the heat of formation of SnF_4 and Br_2-BrF_3 mixture the heats of formation of monoclinic and orthorhombic stannous fluoride are -160.3 ± 1.3 and -142.2 ± 1.3 kcal./mole respectively. The anticipated value was -138 kcal./mole, viz. the heat of formation of $Sn(OH)_2$. The differences between the heats of formation of the two compounds was expected to be approximately 5 kcal. The value for the orthorhombic form appears to be correct, by comparison with ΔH_f $Sn(OH)_2$, but the value for the monoclinic form is suspect. However this calorimetric technique is suitable to detect heat differences of 3 kcal./mole between the two forms.

Applications of bromine trifluoride as a reaction calorimetric liquid.

The reactions with bromine trifluoride can be divided into two categories, those involving ionic reactions and the other concerned with the fluorinating properties of the trifluoride.

a) Ionic reactions in bromine trifluoride.

Neutralisation reactions in pure bromine trifluoride provides the most useful method for determining the heats of formation of ternary fluorides. The heats of formation of the acids and bases in bromine trifluoride have to be determined and by assuming or measuring the heat of neutralisation values for

ternary fluorides are obtained. Combination of the acids and bases listed below would yield the heats of formation of numerous complexes. However many of the compounds formed, when isolated contain bromine trifluoride due to solvolysis.

Bases			Acids		
Monobasic		Dibasic	Mono-acid		Di-acid
Li^{I}	Cs^{I}	Ca^{II}	Au^{III}	Bi^{V}	Ge^{IV}
Na^{I}	Ag^{I}	Sr^{II}	B^{III}	V^{V}	Sn^{IV}
K^{I}	NO^{I}	Ba^{II}	Mn^{IV}	Nb^{V}	Ti^{IV}
Rb^{I}	$NO_2{}^{I}$		P^{V}	Ta^{V}	Pt^{IV}
			As^{V}	Ru^{V}	Pd^{IV}
			Sb^{V}	Os^{V}	
			Ir^{V}		

b) Fluorination reactions with bromine trifluoride.

For those fluorinations which can be effected by both fluorine and BrF_3 the choice of method is governed by balancing the precision required against the effort to achieve it. Thus fluorine bomb calorimetry is the more precise, but bromine trifluoride solution calorimetry is less hazardous and requires simple and cheap equipment.

Some examples of heats of formation that could be obtained by reaction calorimetry in bromine trifluoride are listed below:

1) Gaseous fluorides, (e.g.) AsF_5 and GeF_4

The heats of formation of these compounds could be obtained by reacting the metals with bromine-bromine trifluoride mixture. The value for AsF_5 could be determined by breaking $AsF_{3(liquid)}$ under Br_2-BrF_3 which would be a more moderate reaction than with arsenic metal. Having redetermined the heat of formation of $GeF_{4(g)}$ by the heat of reaction of the metal or dioxide with

bromine-bromine trifluoride, or using the previously reported value[7], the unknown heat of formation of GeF_2 could be obtained from the following reaction heat.

$$3GeF_2 + 2BrF_3 = 3GeF_4 + Br_2 \text{ in } Br_2\text{-}BrF_3$$

2) Fluorides soluble in BrF_3, (e.g.) SnF_4 and SbF_5

The heat of formation of these two compounds have been reported earlier in this chapter. These values could also be obtained from fluorine bomb calorimetry although SnF_4 might form a protective layer on the tin so that analysis would be required. However reaction calorimetry in Br_2-BrF_3 is a most suitable method to determine the unknown heats of formation of SbF_5 and SnF_4. This method, reacting the metal with Br_2-BrF_3, is suitable for any fluorides which are not formed quantitatively in fluorine bomb calorimetry but are soluble in bromine trifluoride.

3) Fluorides insoluble in BrF_3, (e.g.) HgF_2

Despite being insoluble in bromine trifluoride the heats of formation could be obtained by reacting mercurous or mercuric iodate with Br_2-BrF_3 mixture. Woolf[4] obtained 100% oxygen evolution when reacting mercurous iodate with BrF_3 forming insoluble mercuric fluoride and iodine pentafluoride. The stoichiometric reaction is probably due to the formation of iodine pentafluoride which is soluble in BrF_3, and oxygen is evolved.

$$3HgIO_3 + 7BrF_3 = 3IF_5 + 3HgF_2 + 4.5O_2 + 3.5Br_2$$

The heat of formation of mercuric iodate, which is insoluble in water, could be determined by the heat of reaction of aqueous potassium iodate with a soluble mercuric salt, (e.g.) mercuric acetate. This method could be used to determine the heats of

formation of a large number of fluorides including some rare earth trifluorides which might form incompletely from the metal in the fluorine bomb.

4) The heats of formation of iodides that cannot be determined from the heat of reaction of the elements can be obtained by the reaction of the iodide with BrF_3, (e.g.) lower iodides of the transition elements.

5) Reaction calorimetry in bromine trifluoride can be used to obtain unknown or suspect values for chlorides, bromides, oxides, chalcogenides or oxy salts provided the stoichiometry of the reaction has been established.

6) Ternary and quaternary fluorides. As mentioned previously a large number of ternary and quaternary fluorides can be obtained by neutralisation reactions in bromine trifluoride. However the heats of formation of other ternary and quaternary fluorides can be obtained by displacement fluorination reactions with bromine trifluoride. (e.g.) The heat of formation of chloryl fluoride could be obtained by the reaction of $KClO_3$ with BrF_3 (5)

$$6KClO_3 + 10BrF_3 = 6KBrF_4 + 2Br_2 + 3O_2 + 6ClO_2F$$

An interesting application of reaction calorimetry in bromine trifluoride would be to determine the heats of formation of the two forms of $AsCl_2F_3$ and PCl_2F_3. These two compounds exist in covalent and ionic forms, $AsCl_4^+AsF_6^-$ and $PCl_4^+PCl_6^-$.

Some of the applications of reaction calorimetry are listed above. However provided the stoichiometry of the reaction has been established calorimetry in bromine trifluoride can be extended to determine the heats of formation of a large number of fluorides. Stein in a recent review provides a comprehensive

report on reactions with bromine trifluoride.

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APPENDIX I

The heat of formation of arsenic trifluoride.

The heat of formation of arsenic trifluoride was obtained by measuring the heat of hydrolysis with sodium hydroxide solution.

$$2AsF_3 + 6NaOH = As_2O_{3aq.NaOH} + 6NaF_{aq.NaOH} + H_2O$$

This reaction heat was measured to test the calorimetric technique used, but since the values obtained differed from those reported previously[3], the calorimetric technique was checked with the standard reactions outlined in Chapter I. Agreement was satisfactory, and hence the revised heats of reaction were then used to redetermine the heat of formation of arsenic trifluoride.

Materials.

Arsenic trifluoride was prepared by the interaction of calcium fluoride, arsenious oxide and sulphuric acid.

The trifluoride was purified by distillation from sodium fluoride under vacuum and the mid fraction collected in thin-walled glass ampoules. AnalaR sodium fluoride and arsenious oxide were finely ground.

All measurements were made in the Dewar-type calorimeter.

Heat of neutralisation of arsenic trifluoride with N sodium hydroxide.

Wt. AsF_3 (g.)	Wt. NNaOH (g.)	H_2O/AsF_3 (mole ratio)	Heat evolved/mole AsF_3 neutralised (kcal.)
1.7863	259.2	1040	59.19
1.2618	259.4	1520	59.16
1.3924	258.9	1330	59.19
2.7481	259.0	670	59.05
2.1924	258.9	840	59.04

Mean 59.13 ± 0.07

The purity of arsenic trifluoride was confirmed by analysis (See appendix III).

Heat of solution of $As_2O_3/6NaF$ in N NaOH

Wt. $As_2O_3/6NaF$ (g.)	Wt. NNaOH (g.)	Heat evolved/(As_2O_3 + 6NaF) dissolved (kcal.)
4.4003	259.0	10.36
2.1509	261.1	10.58

Mean 10.47 ± 0.11

The heat of solution of As_2O_3 in aqueous sodium hydroxide has been measured previously by Mortimer et. al.[4] and Long with Sackman[5] who obtained values of +12.03, $\pm$0.04 and 12.16 ± 0.10 kcal./mole respectively. The heat of reaction, $NaF \longrightarrow NaF1000H_2O$ is -0.20 kcal./mole and the calculated heat of solution of $As_2O_3/6NaF$ = 10.86 kcal. This is in reasonable agreement with the measured value. The above heats of reaction combined with $-\Delta H_f, As_2O_3$ = 160.30 ± 0.22; $NaOH55H_2O$ = 112.4[6] and NaF = 137.8[7] yield $-\Delta H_f$ AsF_3 = 204.9 kcal./mole. This value is more negative than that reported by Yost

and Sherborne[3] -198.3 kcal./mole.

APPENDIX II

Thermodynamic functions used in Chapter II.

1) Enthalpy of formation (kcal./mole)

All heats of formations were determined at 298°K. To obtain heats of formation at temperature T, Kirchoff's equation was used

$$\Delta H_T = \Delta H_{298} + \int_{298}^{T} Cp\, dT$$

Cp - Heat Capacity, ΔH_{298} - Heat of formation at 298°K and ΔH_T the heat of formation at temperature T.

2) Entropy of formation (cal./deg./mole)

Entropies of formation were calculated from the standard entropies of the compounds involved

$$\Delta S_f^o = S^o_{T(Compound)} - \Sigma S^o_{T(Component\ of\ elements)}$$

ΔS_f^o - Entropy of formation, S_T^o - Standard entropy at temperature T.

e.g. Calculation of entropy of formation of fluorosulphuric acid at 298°K

$S^o_{HSO_3F(g)} = 71.4$ (Savoie and Giguere[1])

$$\Delta S^o_{f HSO_3F} = S^o_{HSO_3F(g)} - \left[S^o_{\frac{1}{2}H_{2(g)} + \frac{1}{2}F_{2(g)} + \frac{3}{2}O_{2(g)} + S_{(s)}} \right]$$

$$= 71.4 - \left[\frac{31.21}{2} + \frac{48.5}{2} + \frac{3 \times 49.02}{2} + 7.62 \right] = -49.60$$

$\Delta S^o_{f HSO_3F} = -49.60$, $\Delta S^o_{f HSO_3F_{(l)}} = -71.6$ assuming

Trouton's Constant = 22

Similarly other entropies of formation were calculated. Standard entropies of fluoro- and chloro-sulphuric acid at their boiling points were calculated by statistical thermodynamics.

The free energy functions were calculated from spectroscopic

data reported by Savoie and Giguere.

For any free energy function X

$$X = X_{\text{translational}} + X_{\text{rotational}} + X_{\text{vibrational}} + X_{\text{internal rotation}}$$

To calculate standard entropy the free energy functions

$(\frac{H^\circ - E^\circ_o}{T})$ and $-(\frac{G^\circ - E^\circ_o}{T})$ were required.

a) Contribution of translational energy to free energy funtions.

For gaseous molecules $E^\circ_o = 0$

i.e. $-(\frac{G^\circ - E^\circ_o}{T})_{trans} = -(\frac{G^\circ}{T})$

and $(\frac{H^\circ - E^\circ_o}{T})_{trans} = (\frac{H^\circ}{T})$

this also applies to rotational energy.

Enthalpy term $\frac{H^\circ}{T} = \frac{5R}{2}$

and Gibb's free energy

$$\frac{-G}{T} = R\left[\frac{5}{2}\ln T - \ln P + \frac{3}{2}\ln M - 3.6647\right]$$

$$S^\circ = R\left[\frac{5}{2}\ln T - \ln P + \frac{3}{2}\ln M - 1.1647\right]$$

M - Atomic Weight, P - Atmospheres, T - ($^\circ$K)

b) Contribution of rotational energy to free energy functions.

Once again $E^\circ_o = 0$

$$\frac{H^\circ}{T} = \frac{3R}{2}$$

and $$\frac{-G^\circ}{T} = R\left[\frac{3}{2}\ln T + \frac{1}{2}\ln ABC - \ln\sigma + 133.1867\right]$$

$$S^\circ = R\left[\frac{3}{2}\ln T + \frac{1}{2}\ln ABC - \ln\sigma + 134.6867\right]$$

ABC are the principal moments of inertia in the molecule and those calculated by Savoie and Giguere were used. σ is the number of equivalent positions of the molecule which can be

produced by rotation of the molecule about an axis of symmetry. For fluoro- and chloro-sulphuric acid σ is unity, hence $\ln\sigma = 0$.

c) Contribution of vibrational energy to free energy functions.

This is obtained from the summation of terms for each fundamental frequency as calculated from Einstein functions. This treatment is valid whenever the rotational and vibrational partition functions are separable and the vibration is simple harmonic. The results are tabulated giving enthalpy function $(\frac{H^\circ - E^\circ}{T})_o$ and Gibbs free energy function $(\frac{G^\circ - E^\circ}{T})_o$ for various values of $\frac{\tilde{\nu}}{T}$

$\tilde{\nu}$ - Wave numbers and the thermodynamic quantities are in cal./mole/deg. T - $^\circ$K

d) Contribution of internal rotation to free energy functions.

Free energy functions are tabulated against $\bar{V}_o/RT$ for various value of $1/r_m$

r_m is the partition function for the n^{th} internally rotating group. These partition functions are given by the relation

$$r_m = \left(\frac{8\pi^3 I_m kT}{nh}\right)^{1/2} = \frac{2.7935(10^{38} I_m T)^{1/2}}{n}$$

T = $^\circ$K; $I_m = I_{OH} = 1.66 \times 10^{-40}$ (g.cm^2) as reported by Savoie and Giguere.

n - number of exchanges of identical atoms which can be brought about by internal rotation. Strictly speaking the necessity for introduction of the factor n arises in the same way that σ enters the above equation.

$\bar{V}_o$ = 1320 cal/mole

To check the technique used, the free energy functions calculated by Savoie and Giguere for HSO_3F and HSO_3Cl were

re-determined.

Calculation of enthalpy and free energy functions of fluorosulphuric acid at its b.p.(436°K)

This assumes monomeric HSO_3F and HSO_3Cl in the vapour state and that the infrared spectra at the b.p. will be similar to that at room temperature. However this will make little difference to enthalpy and free energy functions calculated.

a) Translational contribution

$$\frac{H^\circ}{T} = \frac{5R}{2} = \frac{1.987 \times 5}{2} = 4.97 \text{ cal. deg}^{-1}$$

$$-\frac{G^\circ}{T} = 1.987\left[2.303 \times \frac{5}{2}\log 436 - \ln 1 + \frac{3}{2} \times 2.303 \times \log 100.07 - 3.664\right]$$

$$= 1.987[15.21 + 6.91 + 3.667] = 36.68 \text{ cal. deg}^{-1}$$

$$-G^\circ/_T = 36.68 \text{ cal. deg}^{-1}$$

b) Rotational contribution

$$\frac{H^\circ}{T} = \frac{3R}{2} = 2.98 \text{ cal. deg}^{-1}$$

$$-\frac{G^\circ}{T} = 1.987\left[\frac{3}{2} \times 2.303 \times \log 436 + \frac{1}{2}\log(166 \times 161 \times 165 \times 10^{-120})\right] \times 2.303 + 133.186$$

$$= 1.987[9.12 - 130.53 + 133.186] = 23.42 \text{ cal. deg}^{-1}$$

$$-\frac{G^\circ}{T} = 23.42 \text{ cal. deg}^{-1}$$

c) Internal Rotation

$$\tilde{\nu}_o/_{RT} = \frac{1320}{1.987 \times 436} = 1.52$$

$$1/r_m = 0.161$$

$$\left(\frac{H^\circ - E^\circ}{T}o\right) = 1.63 \text{ cal. deg}^{-1} \quad \left(\frac{G^\circ - E^\circ}{T}o\right) = 0.89 \text{ cal. deg}^{-1}$$

d) Vibrational contribution

$\bar{\nu}$	$\bar{\nu}/_{436}$	$(\frac{H^\circ - E^\circ_o}{T})$	$-(\frac{G^\circ - E^\circ_o}{T})$
3603	8.30	0	0
1243	2.85	0.138	0.031
1151	2.64	0.173	0.045
955	2.19	0.277	0.086
896	2.06	0.325	0.107
550	1.26	0.717	0.360
410	0.94	0.930	0.585
390	0.89	0.971	0.636
1486	3.41	0.074	0.015
561	1.29	0.667	0.333
		Total 4.282	Total 2.098

Contribution	$(\frac{H^\circ - E^\circ_o}{T})$	$-(\frac{G^\circ - E^\circ_o}{T})$
Translational	4.97	36.68
Rotational	2.98	23.42
Internal Rotation	1.63	0.89
Vibrational	4.28	2.10
	Total 13.86	Total 63.09

Thus for fluorosulphuric acid at 435°K

$$(\frac{H^\circ - E^\circ_o}{T}) = 13.86\ cal.\ deg^{-1} \quad -(\frac{G^\circ - E^\circ_o}{T}) = 63.09\ cal.\ deg^{-1}$$

and $S^\circ = 76.95\ cal.\ deg^{-1}$

The standard entropies of other compounds at the b.p.'s were also calculated from free energy functions.

3) Calculation of Gibbs free energy of formation

$$\Delta G^1 = \Delta H - T\Delta S$$

4) Determination of equilibrium constant

$$\Delta G^{\circ} = -RT\ln K$$

ΔG° - free energy of reaction = free energy of formation of products-free energy of formation of reactants.

Kapustinskii's equation.

The lattice energies of fluorosulphates were calculated from this equation and the values obtained used to calculate the heats of formation of other fluorosulphates by comparison with potassium fluorosulphate.

$$U = 287.2 \sum n \frac{z_1 z_2}{r_c + r_a} \left(1 - \frac{0.345}{r_c + r_a}\right)$$

U - lattice energy; n - number of ions/mole of the crystal; $z_1 z_2$ - ionic charges of cation and anion; r_a and r_c - are the radii of the cation and the anion.

It can be seen that the lattice energy of fluorosulphates depends on the size of the cation since the anion size is fixed. The effective radius of the fluorosulphate ion (2.40Å) has been measured in metal hexammine fluorosulphates. The choice of the appropriate cation radii to be used for non-spherical ions could lead to error. For metal cations the Pauling crystal radii are used. The value used for NO^+ is 1.06Å and an error of 0.1Å in this value would alter the lattice energy by 4.0 kcal.

Calculation of the entropy of the aqueous fluorosulphate ion.

This value was obtained from the empirical equation derived by Couture and Laidler. A weighted-mean interatomic distance of 1.47Å was used for the ion. A recent X-ray structural determination of KSO_3F gave S-O lengths of 1.43Å and S-F of 1.58Å.

$$S^{o}_{abs.} = 40.2 + (\tfrac{3}{2})R\ln M - \frac{27.2z^2}{0.25n \times r}$$

S^{o}_{abs} is the entropy relative to a value of -5.5e.u. for the proton; M is the molecular weight; z the number of charges on the ion; n number of charge bearing ligands; r is equal to r_{12} + 1.40 where r_{12} is the interatomic distance between the central atom and the surrounding oxygens and 1.40 is the van der Waals radius of oxygen.

APPARATUS FOR ELECTROMETRIC DETERMINATION OF CHLORINE

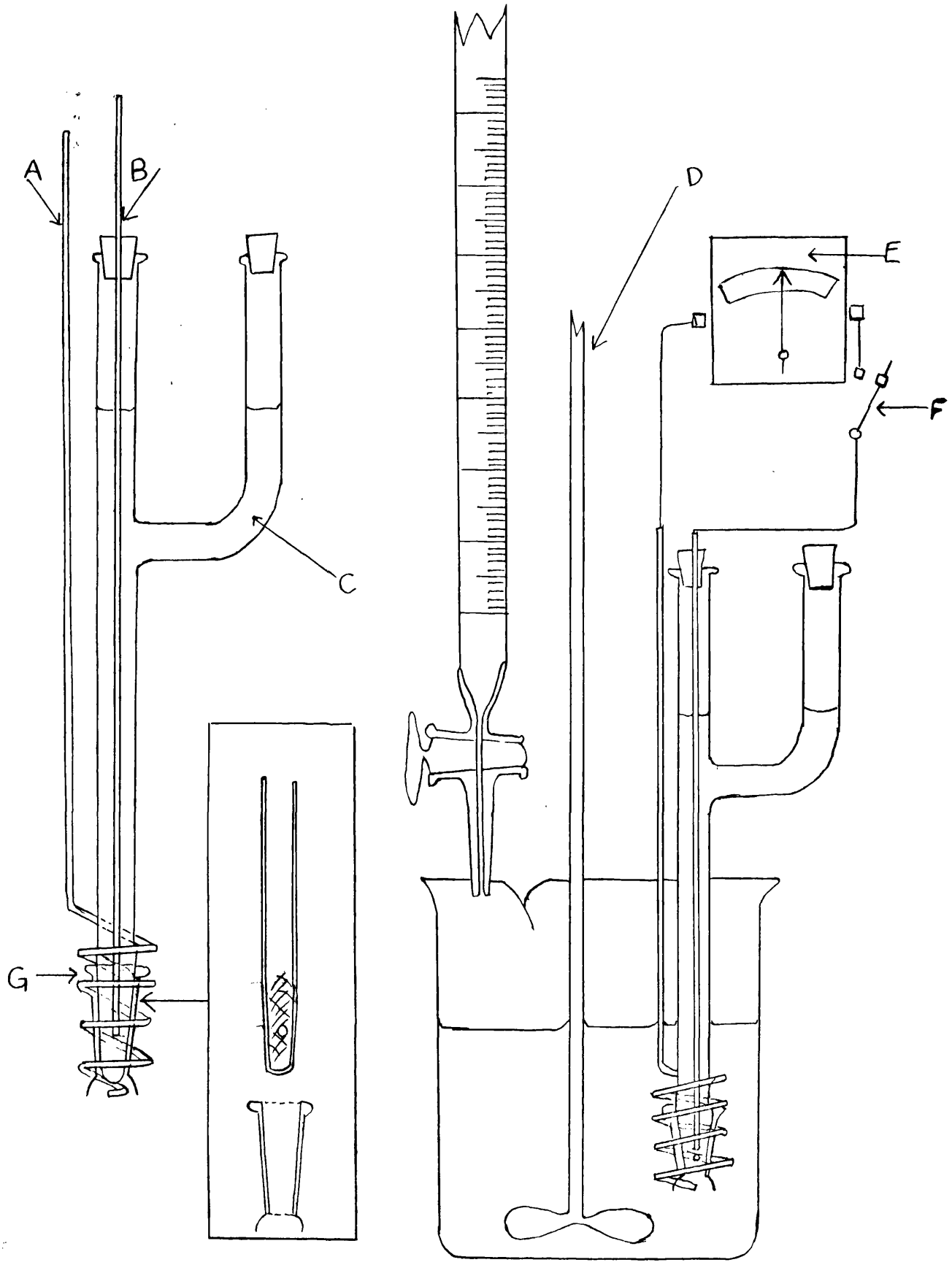

Fig. 10.

APPENDIX III

Analytical Methods.

Arsenious oxide

Sodium arsenite was formed by the hydrolysis of arsenic trifluoride with sodium hydroxide. The excess sodium hydroxide was neutralised with 2N sulphuric acid and $NaHCO_3$ was added until the solution became saturated. The trivalent arsenic was titrated with iodine and starch indicator until the purple colour persisted for at least 30 seconds.

Chlorine[2]

This was determined by an electrometric method involving titration with standard silver nitrate solution using the apparatus shown opposite. This comprised of an end point cell, the silver/silver chloride electrode B and a silver electrode A, each soldered to copper wire and connected in series with a centre-zero micro-ammeter E and tapping key F. The end point cell was made from a glass tube 1cm. o.d. and 20cm. long containing 3×10^{-5}N $AgNO_3$ in 0.1N HNO_3(C); solution C leaked slowly through the small hole in an extended B10 cone covered by a B10 socket sleeve G around which A was wound to locate it. The mixture was well stirred by an electrically driven glass stirrer. The silver/silver chloride electrode was prepared by making a degreased, acid etched length of 16SWG silver wire, the anode in the electrolysis of a N sodium chloride solution using a platinum wire cathode. The process was carried out for eight hours at 2v. and 2.5mA.

The acidity of the halide solution was adjusted to 0.1N with respect to nitric acid using 8N for which about 1.2ml./100ml. of

solution was required. Standard silver nitrate solution was titrated into this solution, F being depressed after each addition and the end point detected at zero deflection on E.

For the determination of chloride, the apparatus functions as a concentration cell, containing two opposing silver/silver chloride electrodes; E = 0 volts; and the e.m.f. in the circuit arises from the difference in the concentration of silver ions surrounding each electrode (C_{Ag^+}). During the titration silver chloride is precipitated, the solution being saturated with it, and $C_{Ag^+} = L_s^{\frac{1}{2}}$, where L_s is the solubility product of silver chloride, 2×10^{-25} so that $C_{Ag^+} = 1.4 \times 10^{-5}$ eq./litre in the titrate, compared with 3×10^{-5} eq./litre in the end point cell. Beyond the end point, addition of silver nitrate raises the C_{Ag^+} above $L_s^{\frac{1}{2}}$ and above 3×10^{-5} eq./litre which corresponds to zero deflection so that the presence of excess silver ion reverses the direction of the e.m.f. and the deflection on E.

Fluorine

Fluorine was separated by distillation of a sulphuric acid solution in the presence of silica. Fluorosilicic acid is the volatile product.

Reagents:-

(a) Sodium alizarin sulphonate, 0.1g. in 200ml. shake at intervals for several hours and filter;

(b) $^{N}/_{10}$ $Th(NO_3)_4$ solution;

(c) $^{N}/_{10}$ NaF solution;

(d) 50% H_2SO_4;

(e) soft glass wool;

(f) $^{N}/_{20}$ HCl;

(g) 2% NaOH solution;

(h) Buffer solution, 9.45g. chloroacetic acid + 2.00g. NaOH in 100ml. H_2O.

Method:- A sample containing 10-50mg. F^- was placed in a flask with glass wool, glass beads and 40ml. (50% H_2SO_4). The flask was fitted up for steam distillation with the bulb of the thermometer approximately 1cm. from the base of the flask. When the temperature reached 135-140° steam distillation was commenced and 75ml. was collected. To ensure that all fluorosilicic acid had been collected another 50ml. was collected when the temperature was greater than 135°. The solution was diluted with 100ml. of water and sodium alizarin sulphonate added. The acidity was adjusted with the sodium hydroxide and hydrochloric acid solutions leaving the solution just acid and the pink colour discharged. 1ml. buffer was added and the mixture was titrated with $^N/_{10}$ $Th(NO_3)_4$ solution. The $Th(NO_3)_4$ solution was standardised by repeating the distillation with sodium fluoride solution.

Hydrogen fluoride

The amount of hydrogen fluoride in the electrolyte from the fluorine cell was determined by weighing approximately 1g. electrolyte in a platinum dish, adding boiled out water and titrating with $^N/_1$ NaOH using phenolphthalein as indicator.

Nitrogen

Nitrogen was determined by conversion to ammonia by Devarda's alloy (50Cu, 45Al, 5Zn) in strongly alkaline solution.

The nitrogen containing compound was dissolved in 240ml. water. 3g. finely divided Devarda's alloy was added then 10ml. 20% sodium hydroxide, and the solution was warmed gently to start the reaction. The apparatus was allowed to stand for 1 hour to

ensure complete reduction. The ammonia was distilled into 100mls. standard hydrochloric acid until only 40-50ml. remained in the distillation flask. The condenser was washed with a little distilled water and the contents of the receiver titrated with standard sodium hydroxide using methyl red as indicator.

Potassium

This was determined by evaporating a solution of the potassium salt in sulphuric acid to dryness in a platinum dish. This operation was repeated twice. The mixture was then heated to 400-700° for 15 minutes. The platinum dish was allowed to cool in a desiccator and the process repeated until a constant weight of potassium sulphate was obtained.

Potassium iodate

Potassium iodate is formed by the hydrolysis of iodine pentafluoride with aqueous potassium hydroxide. The amount of KIO_3 in solution was determined by neutralising the mixture with 2N sulphuric acid, adding excess KI and titrating the liberated iodine with standard sodium thiosulphate using starch as indicator.

Silver

This was determined gravimetrically as the chloride. A solution of the salt (200ml.) containing approximately 0.1g. silver and 1% by volume of nitric acid was heated to 70° and 0.2N hydrochloric acid added until no further precipitation occurred. The mixture was warmed until the precipitate settled and the liquid tested for complete precipitation. The precipitate was allowed to settle overnight in the dark. The supernatent liquid was filtered off and the precipitate washed by decantation

with 0.1N nitric acid. The precipitate was transferred to a Gooch crucible and washed with 0.01N nitric acid until free from chloride and dried at 130° until constant weight was obtained.

Sulphur

Sulphur was determined gravimetrically as barium sulphate. If fluoride was also present it was removed by evaporation to dryness three times with hydrochloric acid.

An amount of compound containing 0.05 to 0.06g. sulphur was dissolved in 25ml. water to which was added 0.3 to 0.6ml. concentrated hydrochloric acid and the solution was diluted to approximately 200ml. The solution was boiled and 10-12ml. 5% $BaCl_2$(0.2M) was added dropwise while stirring the solution. The precipitate was allowed to settle and the supernatent liquid tested for complete precipitation. The solution was digested for approximately one hour, or left overnight, to obtain a granular precipitate. The precipitate was filtered on to a tared porcelain crucible then washed with warm water until washings contained no chloride ions. The precipitate was dried at 110° and heated to 600°.

T.H.A.M.

The purity of T.H.A.M. was determined by titration with 0.1N hydrochloric acid using a 1:1 solution of 1% Alizarin red S and Bromocresol green as indicator

Tin

Tin was determined by heating the salt with 2-3ml. concentrated nitric acid, the excess acid was evaporated and the residue ignited and SnO_2 was weighed.

Titanium

This was determined by conversion to the oxide which was

weighed. The titanium was precipitated by boiling the ammonia solution of the salt. The precipitate was calcined above 700° and weighed as TiO_2.

Qualitative test for MoF_6.

800mg. Mo (3 x 230mg. quantities) were reacted with 45g. Br_2-BrF_3 solution in the twin-cell calorimeter forming MoF_6 (b.p. 35°). MoF_6 has little interaction with BrF_3 and if present in the mixture would distil off before bromine-bromine trifluoride. The mixture was distilled under vacuum until Br_2 obtained. The mixture obtained from the distillation was reacted with carbon tetrachloride in a closed system. Sodium hydroxide solution was added and CCl_4 distilled off. Sn/HCl and KCNS was then added; no red colour was obtained. If there were $<$ 1% MoF_6 remaining in solution the heat correction to be applied would be negligible, so the test was repeated with Na_2MoO_4 (equivalent to 8mg. Mo) and a red colour formed. Thus $<$ 1% Mo remained in the Br_2-BrF_3 mixture after the reaction.

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